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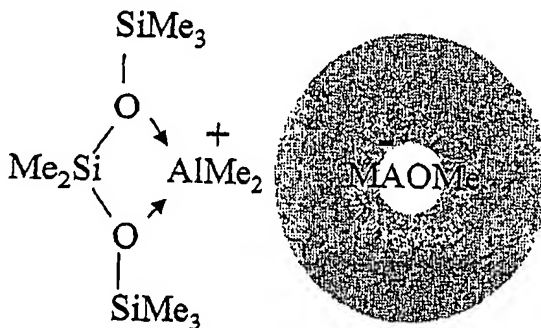
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(54) Title: IONIC ALUMINOXANATE COMPOSITIONS AND THEIR USE IN CATALYSIS

### DiMethylAluminum Methaluminoxanate



(57) Abstract: Ionic aluminoxanates are provided. Unlike conventional aluminoxanes the aluminoxanates are highly electrically conductive, e.g., when dissolved in methylene chloride. They can be used in supported, unsupported, or self-supported form as polymerization catalysts with all known transition metal olefin polymerization catalyst compounds or complexes. The ionic aluminoxanates can be made by (A) thoroughly washing a liquid clathrate formed from (i) an aluminoxane, (ii) an organic, inorganic, or organometallic compound, and (iii) an organic solvent to form a washed liquid clathrate; (B) mixing an inert liquid non-solvent with viscous liquid clathrate from (A) to form a slurry comprised of precipitated solids and a liquid phase; and (C) recovering precipitated solids from the liquid phase, these being the ionic aluminoxanates. Other methods are described for making and/or recovering the ionic aluminoxanates.

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## **IONIC ALUMINOXANATE COMPOSITIONS AND THEIR USE IN CATALYSIS**

[0001] The work leading to the invention described in this patent application was performed pursuant to a contract with an agency of the United States Government. The contract is Cooperative Agreement No. 70NANBOH3049 between Albemarle Corporation and the National Institute of Standards and Technology of the United States Department of Commerce (Advanced Technology Program).

### **TECHNICAL FIELD**

[0002] This invention relates to new ionic compositions that are of particular utility in the formation of new catalyst systems, to methods for the preparation of these ionic compositions and catalyst systems, and to the use of such catalyst systems in the polymerization (homopolymerization and copolymerization) of olefins or the like.

### **BACKGROUND**

[0003] U.S. Pat. Nos. 5,670,682 and 5,922,631, the disclosures of which are incorporated herein, describe the formation of liquid clathrates of aluminoxanes and the use of such materials as components in the formation of certain olefin polymerization catalysts. U.S. Pat. No. 5,565,395 describes aluminoxanate compositions formed by reacting hydrocarbylaluminoxanes with certain salts of polyoxy compounds. In some cases transient clathrate formation was observed.

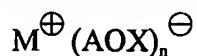
### **BRIEF SUMMARY OF THE INVENTION**

[0004] It has now been discovered that the liquid clathrates of the types described in U.S. Pat. Nos. 5,670,682 and 5,922,631 can be used as starting materials for the formation of ionic aluminoxanate compositions. These new compositions are highly efficient as well as highly effective as cocatalysts with a wide variety of transition metal catalysts. For example, these new compositions do not require use of large excesses of aluminum to transition metal as is the case with ordinary aluminoxane or previously known "modified" aluminoxane cocatalyst compositions. In fact at least some of the new compositions of this invention effectively function in olefin catalysis using molar aluminum:transition metal ratios as low as 20:1. Moreover at least some of the new compositions of this invention have the ability to provide polyolefin polymer of very narrow polydispersity even when the transition metal compound is a Ziegler-Natta catalyst compound such as a simple transition metal halide or alkoxide or mixed halide-alkoxide of a transition metal. Another feature of the new compositions of this invention is that they tend to be significantly more effective when used in combination with late transition metal catalysts or titanium compounds or complexes than conventional aluminoxanes or conventional "modified" aluminoxanes.

[0005] Thus, in one of its embodiments this invention provides new ionic compounds

derived from aluminoxanes, which new compounds are herein termed ionic aluminoxanates. The ionic aluminoxanates of this invention are substantially free of occluded non-ionic organoaluminum compounds such as aluminum alkyls and non-ionic alkylaluminoxane species. By this is meant that the ionic aluminoxanate contains, if any, less than 5 mole percent, preferably less than 2 mole percent, and more preferably less than 1 mole percent of aluminum as aluminum trialkyl as determined by proton NMR. That is, of the total aluminum content of the compound, if any is present in the form of aluminum trialkyl, the amount of aluminum as aluminum trialkyl is less than the mole percentage specified. Suitable procedures for conducting such proton NMR analyses are described by D.W. Imhoff, L.S. Simeral, D.R. Blevins, and W.R. Beard, "Determination of Trimethylaluminum and Characterization of Methylaluminoxanes Using Proton NMR", *Olefin Polymerization: Emerging Frontiers*, ACS Symposium Series 749, P. Arjunan, J.E. McGrath, T.L. Hanlon, eds., American Chemical Society, 2000, pp. 177-191. See also D.W. Imhoff, L.S. Simeral, S.A. Sangokoya, J.H. Peel, "Characterization of Methylaluminoxane and Determination of Trimethylaluminum Using Proton NMR", *Organometallics*, 1998, 17, 1941. If an ionic aluminoxanate produced as described herein is shown by proton NMR to have, if any, such a low level of aluminum trialkyl, it is a certainty that the ionic aluminoxanate has no occluded non-ionic aluminoxane species, because removal of aluminum trialkyl from an ionic aluminoxanate in the manner described herein ensures removal of occluded non-ionic aluminoxane species as well. This is borne out by the fact that the electrical conductivity at 25°C of an ionic aluminoxanate of this invention when dissolved to a concentration of 1.67 weight percent in 99.9% A.C.S. HPLC grade, or better, methylene chloride, is significantly higher than the electrical conductivity, under the same conditions, of the aluminoxane from which the ionic aluminoxanate is derived. By "significantly higher" is meant that the conductivity of the ionic aluminoxanate under these test conditions is at least 70 micro-mhos higher than the conductivity under the same test conditions of the aluminoxane from which the aluminoxanate was formed.

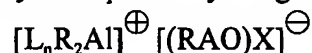
[0006] One type of ionic aluminoxanate is an ionic aluminoxanate of the formula:



where M is a Group 1 or 2 metal atom, a tetrahydrocarbylammonium group, a tetrahydrocarbylphosphonium group, a trityl group; AO is an aluminoxane moiety; X is a leaving group from a compound, MX; and n is the valence of M. Thus this type of ionic aluminoxanate is a salt having a cation, M, and an anion, AOX, composed of at least one aluminoxane moiety, AO, coordinated with a leaving group from a compound, MX, used as a raw material from which the ionic aluminoxanate product is derived. An example is potassium methylaluminoxanate,  $K^{\oplus} MAOCl^{\ominus}$ , which can be formed from a clathrate formed from KCl, methylaluminoxane, and an aromatic solvent by processing described

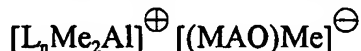
hereinafter. Another example is lithium aluminoxanate,  $\text{Li}^{\oplus} \text{MAOBu}^{\ominus}$ , which can be formed from a clathrate formed from BuLi, methylaluminoxane, and an aromatic solvent by processes described hereinafter. U.S. Pat. No. 5,565,395 describes the production of these and many other clathrates useful in forming ionic aluminoxanates of this first type.

[0007] Another type of ionic aluminoxanates of this invention is a chelated dihydrocarbylaluminum aluminoxanate which is salt having a chelated dihydrocarbylaluminum group as the cation and an aluminoxanate moiety as the anion. These constitute a more preferred type of ionic aluminoxanates. Surprisingly, such chelated dihydrocarbylaluminum aluminoxanates are capable of activating metallocene halides, e.g.,  $\text{Cp}_2\text{ZrCl}_2$ , as well as metallocene alkyls, e.g.,  $\text{Cp}_2\text{ZrMe}_2$ . An example of these chelated dihydrocarbylaluminum aluminoxanates is an ionic compound having a cation composed of a polysiloxane ligand coordinated with dihydrocarbylaluminum and an anion composed of an aluminoxane moiety coordinated with a leaving group such as a hydrocarbyl group, a halogen atom, a hydrocarbyloxy group, or the like. These ionic aluminoxanates can be formed from a clathrate formed from an aluminoxane, a linear, branched or cyclic polysiloxane having at least 3 silicon atoms per molecule, and an aromatic hydrocarbon solvent. U.S. Pat. No. 5,922,631 describes the preparation of such clathrates. Another example of these more preferred ionic aluminoxanates is an ionic compound having a cation composed of a monoether or polyether ligand coordinated with dihydrocarbylaluminum and an anion composed of an aluminoxane moiety coordinated with a leaving group such as a hydrocarbyl group, a halogen atom, a hydrocarbyloxy group, or the like. These more preferred ionic aluminoxanates may be depicted by the general formula:



where L is a stabilizing ligand which can be a monosiloxane, polysiloxane, monoether, polyether, monothioether, polythioether, or a multidentate ligand having oxygen, nitrogen, phosphorus, or sulfur coordinating atoms therein or a combination of two or more of such coordinating atoms (preferably L is a polysiloxane, polyether, or oxygen and/or nitrogen crown ether ligand), R is a hydrocarbyl group (e.g., alkyl, cycloalkyl, aryl, aralkyl, etc., preferably a  $\text{C}_{1-8}$  alkyl group, and most preferably a methyl group), X is a hydrocarbyl group, a halogen atom, or a hydrocarbyloxy group, and n is 1 when L is a bidentate ligand and 2 when L is a monodentate ligand. Preferably X is an alkyl group, and most preferably methyl. Preferably L is polysiloxane, polyether, or other bidentate ligand and n is thus 1. The ligand, L, stabilizes the cation of these ionic aluminoxanates. Thus, this invention provides an ionic aluminoxanate salt composition composed of (i) a stabilized dialkylaluminum cation of the formula  $[\text{L}_n\text{R}_2\text{Al}]^{\oplus}$ , where L is a stabilizing ligand, each R is, independently, an alkyl group having up to about 20 carbon atoms and n is 1 when L is a bidentate ligand and 2 when L is a monodentate ligand; and (ii) an aluminoxanate anion of the formula  $[(\text{RAO})\text{X}]^{\ominus}$ , where

RAO is an alkylaluminumoxane in which the alkyl group has up to about 20 carbon atoms and is the same or different from the alkyl group of said cation, and wherein X is an alkyl group which may or may not correspond to the alkyl group of RAO. Preferably, the alkyl groups of the cation of the formula  $[L_nR_2Al]^{\oplus}$ , and of the anion of the formula  $[(RAO)X]^{\ominus}$  are, independently, either a methyl group or an ethyl group, and more preferably such alkyl groups are all methyl groups. In the case of methylaluminumoxane as the aluminumoxane used to prepare these preferred aluminumoxanates, the aluminumoxanate can be represented by the formula:



wherein L is as defined above, Me is methyl, and MAO is methylaluminumoxane.

**[0008]** Particularly preferred ionic aluminumoxanate salt compositions of this invention are those in which the composition has a siloxane or polysiloxane ligand and in which the composition is characterized by a downfield shift of the ligand peaks in  $^{29}Si$  NMR of at least 5 ppm and at least 0.2 ppm downfield shift in  $^1H$  NMR. It is also particularly preferred that the ionic aluminumoxanate salt composition of this invention be further characterized by (i) a  $^{27}Al$  NMR with at least one large and broad peak shifted upfield from the parent aluminumoxane peak, and (ii) at least one smaller peak shifted downfield from the parent aluminumoxane peak. The large and broad peak of (i) corresponds to the anionic aluminumoxanate peak and the smaller peak of (ii) corresponds to the cation of the ionic aluminumoxanate salt.

**[0009]** Especially preferred aluminumoxanate salts of this invention are further characterized by at least a ten micro-mhos increase in conductivity compared to the parent aluminumoxane. As used herein, the term "parent aluminumoxane" refers to the alkylaluminumoxane from which the ionic aluminumoxanate salt has been prepared.

**[0010]** A process for producing the new ionic aluminumoxanates of this invention comprises the following steps:

- I) a stable liquid clathrate -- formed from (i) an aluminumoxane, (ii) an effective amount of an organic, inorganic, or organometallic compound, and (iii) an aromatic organic solvent as in for example U.S. Pat. Nos. 5,670,682 and 5,922,631 -- is thoroughly washed (intimately mixed) one or more times with an aromatic solvent, each time forming a two-phase system composed of a lower layer of a viscous liquid composed of ionic aluminumoxanate and included aromatic solvent, and an upper layer of a less dense liquid, and (A) each time or (B) when two or more washes are conducted, each time except for the last time, the layer of less dense liquid is removed and discarded such that after the last time a two-phase liquid system remains; and
- II) recovering ionic aluminumoxanate solids from the viscous liquid.

To recover the ionic aluminumoxanate solids in step b), any of several different methods can be used:

- 1) In one method, the solids are precipitated from the viscous liquid by mixing a liquid

non-solvent such as a liquid paraffinic or cycloparaffinic hydrocarbon with the viscous liquid. These solids are then isolated by any suitable physical liquid/solids separation procedure such as filtration, centrifugation, decantation, or the like. Preferably, the isolated ionic aluminoxanate solids are then dried, for example, under vacuum and at ambient room temperature. Alternatively, the solids can be recovered by spray drying the viscous liquid, typically at a temperature of up to about 50°C. If desired, prior to conducting the spray drying operation, the viscous liquid can be diluted with a suitable aromatic solvent such as chlorobenzene.

- 2) In another method, the included aromatic solvent is removed by vacuum distillation from the viscous liquid from (A) above or the less dense liquid and the included aromatic solvent are removed by vacuum distillation from the two-phase liquid system remaining from (B) above.

[0011] In one of its embodiments this invention provides a process for producing the new ionic aluminoxanates of this invention comprises the following steps:

- a) thoroughly washing a liquid clathrate formed from (i) an aluminoxane, (ii) an effective amount of an organic, inorganic, or organometallic compound, and (iii) an aromatic solvent, to form a product comprised of a liquid clathrate and solvent; and
- b) removing said solvent from liquid clathrate of A) by vacuum distillation to isolate particulate solids of said ionic aluminoxanate.

[0012] Another embodiment is a process for producing the new ionic aluminoxanates of this invention, which process comprises the following steps:

- a) a stable liquid clathrate formed from (i) an aluminoxane, (ii) an effective amount of an organic, inorganic, or organometallic compound, and (iii) an aromatic organic solvent is thoroughly washed (intimately mixed) one or more times with an aromatic solvent, each time forming a two-phase system composed of a lower layer of a viscous liquid, and an upper layer of a less dense liquid which is removed and discarded;
- b) after removing the upper layer, or the last of the upper layers where two or more washings are conducted in a), an inert liquid non-solvent such as a liquid paraffinic or cycloparaffinic hydrocarbon is mixed with the viscous liquid to form a slurry comprised of precipitated solids and a liquid phase; and
- c) the precipitated solids are recovered from the liquid phase.

The recovered precipitated solids, optionally washed with additional inert liquid non-solvent after recovery, will possess a higher electrical conductivity and are thus more ionic than solids that are precipitated from the initial unwashed clathrate. By "an effective amount" as used herein with reference to step a) of the above process, is meant an amount of the organic, inorganic, or organometallic compound which is sufficient to form a stable clathrate but

insufficient to cause the aluminoxanate to be incapable of inactivating a selected metallocene catalyst of a transition metal including the lanthanide and the actinide series, such as, for example, a Group 4 metallocene catalyst. In other words, if too much (ii) is used relative to (i) and (iii), the resultant aluminoxanate may be unable to activate a given metallocene catalyst of such a transition metal, such as, for example, dicyclopentadienyl zirconium dichloride.

[0013] Optionally, the precipitated solids from step c) are subjected to at least one repetition procedure wherein such precipitated solids from step c) are mixed with fresh aromatic solvent to reform a clathrate, which is then washed as in step a) and the resultant rewashed liquid composition is then subjected to step b), and the resultant precipitated solids are then recovered as in step c). The solids recovered in step c) of this first repetition of the procedure will typically have a still greater electrical conductivity than the solids recovered from the initial step c). If however the electrical conductivity is the same, no further repetition of this optional procedure is indicated. The point here is that this optional repetition procedure can be repeated as many times as desired, until formation of a solid ionic aluminoxanate having a suitably increased electrical conductivity has been achieved, and this is readily determined in any given case by performing a few tests in the laboratory to assess the number of washings and the total volume of aromatic washing solvent relative to a given amount of initial unwashed liquid clathrate that should be used in order to produce an ionic aluminoxanate having the desired properties and characteristics. These are factors which can vary from clathrate to clathrate.

[0014] This invention also provides new supported ionic aluminoxanates in which a stable clathrate is used as a starting material. One way of producing these new supported ionic aluminoxanates involves a process which comprises:

- d) forming and mixing a slurry of (i) an ionic aluminoxanate formed from a stable thoroughly washed liquid clathrate as described above (with or without prior use of one or more optional repetition procedures) and (ii) a particulate catalyst support or carrier material, and (iii) an inert liquid polar halogenated hydrocarbon solvent, or preferably a liquid aromatic hydrocarbon solvent, capable of dissolving the ionic aluminoxanate composition so that (i) (in dissolved or solvated form) and (ii) come into intimate contact with each other and form a supported ionic aluminoxanate.

Optionally, this supported ionic aluminoxanate can be recovered from the mixture formed in d), and if desired can be washed with a liquid diluent inert to the ionic aluminoxanate, and also can then be dried, if desired. It has been found that after the ionic aluminoxanate has been absorbed in the pores of the catalyst support material, the resultant supported ionic aluminoxanate can be contacted (e.g., washed) with an aromatic solvent and yet will not reform a clathrate. Thus when a catalyst support material such as silica or a porous polyolefin



support is used in step d), the liquid diluent used in step d) and the liquid diluent used in the optional subsequent washing of the recovered supported ionic aluminoxanate can be an aromatic solvent. Other types of diluents such as at least one liquid paraffinic or cycloparaffinic hydrocarbon or a mixture of either or both with an aromatic solvent can be used for such washing, if desired.

[0015] The catalyst support or carrier material used in this process can be any particulate material useful as a catalyst support or carrier such as a porous spheroidal or particulate organic resinous support or a porous inorganic support, and preferably is a particulate inorganic catalyst support such as an inorganic oxide or an inorganic material comprised of one or more oxides. It is also preferred that the support be anhydrous or substantially anhydrous. More preferred is a particulate calcined inorganic catalyst such as silica. Also preferred are catalyst supports or carriers which have been chemically treated by known conventional reagents, such as with a suitable aluminum alkyl, *e.g.*, triethyl aluminum, so as to at least remove hydroxyl groups and/or water from the support or carrier. In certain applications, it may be preferred to suspend the carrier material in a viscous inert liquid, *e.g.*, mineral oil. The temperature of the slurry during this process is typically in a temperature range of about 20 to about 80°C, but higher or lower temperatures can be used if desired. Preferably the slurry is at room temperature during the process.

[0016] Also provided by this invention are new polymerization catalyst compositions in which the cocatalyst used is a new ionic aluminoxanate of this invention. These new polymerization catalyst compositions can be used in solution polymerizations or they can be used in supported form in slurry or gas phase polymerizations. In either case while the catalysts have other uses, it is preferred to use the catalysts of this invention as catalysts for the homopolymerization or copolymerization of olefinic monomers such as 1-olefins and vinylaromatic monomers.

[0017] One type of the polymerization catalysts of this invention is an unsupported reaction product between (i) at least one catalyst compound or complex of a transition metal of Groups 3 to 10 of the Periodic Table including the lanthanide and actinide series, and (ii) at least one ionic aluminoxanate of this invention. One way of producing these new catalyst compositions is to form a catalyst in solution by bringing together either in a polymerization reactor or zone or in a separate vessel, at least (i) a catalyst compound or complex of a transition metal of Groups 3 to 10 of the Periodic Table including the lanthanide and actinide series, (ii) an ionic aluminoxanate of this invention, and (iii) a polymerization solvent. These components can be fed separately in any order or any two of them can be premixed and fed as a mixture, with the other component being fed before, during or after the feeding of such mixture to the polymerization reactor or zone or to the separate vessel. If a separate vessel is used, the catalyst formed therein is promptly delivered into the polymerization reactor or

zone. In all cases the customary inert atmospheres and anhydrous polymerization conditions should be observed. The resultant mixture formed in this operation is a solution of a catalyst of this invention in which polymerization of the monomer or combination of monomers is carried out.

[0018] Another type of these new catalyst compositions is a supported catalyst composition of this invention. These compositions are reaction products between (i) a catalyst compound or complex of a transition metal of Groups 3 to 10 of the Periodic Table including the lanthanide and actinide series, and (ii) an ionic aluminoxanate of this invention deposited on a catalyst support or carrier material. These catalyst compositions can be formed in various ways. One method involves depositing the ionic aluminoxanate of this invention on a catalyst support and then mixing the resultant supported aluminoxanate with the transition metal catalyst compound. Another method involves mixing a transition metal catalyst compound with a catalyst support and then contacting the resultant supported transition metal catalyst compound with an ionic aluminoxanate of this invention. Still another method involves mixing together a transition metal catalyst compound and an ionic aluminoxanate of this invention and then contacting the resultant mixture with a catalyst support. Each of these methods is typically conducted in the presence of an inert liquid medium which can be a liquid transition metal compound or complex, but which typically is an inert liquid diluent such as a paraffinic, cycloparaffinic or aromatic hydrocarbon. The foregoing methods are typically carried out at temperatures within the range of about 20 to about 80°C. However, higher or lower temperatures can be used if desired.

[0019] Other embodiments of this invention include methods of polymerizing at least one polymerizable monomer in the presence of a supported or unsupported ionic aluminoxanate of this invention.

[0020] Still other embodiments involve the provision of new stable clathrates which can be used, for example, in forming new ionic aluminoxanate compositions of this invention. These new stable clathrates are formed from (i) an aluminoxane, preferably an alkyl aluminoxane and most preferably methylaluminoxane, (ii) a polyether, or a nitrogen and/or oxygen-containing crown ether, and (iii) an aromatic solvent. These new stable clathrates can be used as starting materials in the various processes described above for forming ionic aluminoxanates of this invention. Also they can be precipitated using non-solvents as described above, to produce solid ionic aluminoxanates of this invention which are highly ionic even if not subjected to the washing procedures described above. And when washed as described above, the ionic character of the ionic aluminoxanates of this invention is still even higher.

[0021] Methods for producing these new stable clathrates constitute further embodiments of this invention.

[0022] Still other embodiments and features of this invention will be still further apparent from the ensuing description and appended claims.

### BRIEF DESCRIPTION OF THE DRAWINGS

[0023] Fig. 1 is a visual representation of one of the preferred chelated ionic aluminoxanates of this invention.

[0024] Fig. 2 are proton NMR spectra of the aluminoxanate of Fig. 1, and of precursors thereof.

[0025] Fig. 3 are  $^{29}\text{Si}$  NMR spectra of the aluminoxanate of Fig. 1, and of precursors thereof.

[0026] Fig. 4 are  $^{27}\text{Al}$  NMR spectra of the aluminoxanate of Fig. 1, and of precursors thereof.

[0027] Fig. 5 are proton NMR spectra of aluminoxanates of this invention having DME or crown-ether as chelates of the dimethylaluminum cation, and the proton spectrum of regular methylaluminumoxane.

[0028] Fig. 6 graphically depicts the results of ethylene polymerizations using a supported catalyst composition of this invention comprised of a late transition metal complex and an aluminoxanate of this invention as compared to polymerizations in which the catalyst composition was made from methylaluminumoxane as the cocatalyst.

### FURTHER DETAILED DESCRIPTION OF THIS INVENTION

#### Ionic aluminoxanates of this Invention

[0029] Stable liquid clathrates used as starting materials in the production of the new ionic aluminoxanates of this invention can be prepared as described in U.S. Pat. Nos. 5,670,682 and 5,922,631, the disclosures of which are incorporated herein. As described therein a wide variety of organic, inorganic, or organometallic compounds are suitable for use in forming the stable clathrates. And, as shown in those patents not every compound will form a stable clathrate. Thus where it has not already been established that a given metal-containing compound will form a stable clathrate, a few preliminary tests using the procedures described in those patents will enable a determination of the suitability of a given metal compound for forming a stable clathrate. As is also disclosed in those patents, a variety of aluminoxanes can be used in forming stable clathrates. Of these, alkylaluminumoxanes are preferred, with methylaluminumoxane being the most preferred material for use in forming the stable clathrates. Methylaluminumoxane is an article of commerce, and methods for preparation of aluminoxanes are reported in the literature. In forming the stable clathrate, the denser lower liquid layer is typically the clathrate, and it is readily separated from the supernatant liquid by conventional separation techniques such as by decantation or draining.

[0030] Preferred stable clathrates for use in as starting materials in the practice of this invention are liquid clathrates which comprise the reaction product, in an aromatic solvent, of (i) a hydrocarbylaluminosiloxane, preferably an alkylaluminosiloxane, and most preferably methylaluminosiloxane, and (ii) a hydrocarbylmonosiloxane, a hydrocarbyldisiloxane, or preferably a hydrocarbylpolysiloxane having at least three silicon atoms in the molecule and which are separated from each other by an oxygen atom such that there is a linear, branched or cyclic backbone of alternating Si and oxygen atoms, with the remainder of the four valence bonds of each of the silicon atoms individually satisfied by a univalent hydrocarbyl group. The hydrocarbylpolysiloxane can have as many as 18 or more silicon atoms in the molecule. The univalent hydrocarbyl groups of the polysiloxane each contain, independently, up to about 18 carbon atoms, and can be such groups as alkyl, cycloalkyl, aryl, aralkyl, etc. Non-limiting examples of such polysiloxanes include hexamethylcyclo-trisiloxane, octamethylcyclotetrasiloxane, octaphenylcyclotetrasiloxane, decamethyltetra-siloxane, dodecamethylpentasiloxane, and tetradecamethylhexasiloxane. A particularly preferred group of clathrates are those formed in a mononuclear aromatic hydrocarbon, such as benzene, toluene, xylene(s), ethylbenzene, cumene, etc., in which the reactants are an alkylaluminosiloxane, most preferably methylaluminosiloxane, and octamethyltrisiloxane. Methods suitable for preparing such clathrates are set forth in U.S. Pat. No. 5,922,631.

[0031] A new type of stable clathrate can be effectively used in forming new ionic aluminosiloxanates of this invention. These new clathrates of this invention are compositions formed from (i) an aluminosiloxane, (ii) an aliphatic or crown polyether, and (iii) an aromatic solvent, wherein the combination of (i), (ii), and (iii) is effective to form a clathrate. Reaction conditions and procedures used for forming these clathrates are analogous to those described in U.S. Pat. No. 5,922,631. These new clathrates are further described hereinafter.

[0032] To form the new ionic aluminosiloxanates of this invention, the clathrate is thoroughly washed with an aromatic solvent such as benzene, toluene, xylene, ethylbenzene, or other aromatic solvent such as a mixture of two or more liquid aromatic hydrocarbons. The volume of aromatic solvent used relative to the initial liquid clathrate is susceptible of variation, and is not critical as long as enough solvent is used to form a stirrable solution. After each washing a two-phase liquid system is formed and the less dense upper layer is separated from denser lower liquid phase, e.g., by decantation. Such washing can be conducted at ambient room temperatures or at suitably reduced or elevated temperatures, e.g., in the range of about 10 to about 100°C although still higher or lower temperatures may be used. More preferably the washing is conducted at one or more temperatures in the range of about 20 to about 80°C. Washing at room temperature is even more preferred in most cases. It is desirable to thoroughly stir or otherwise agitate the mixture formed in the washing. The washing results in the formation of a relatively dense or oily washed liquid clathrate composition. An inert

liquid non-solvent is then added to the clathrate in order to form precipitated solids which should have a reduced content of neutral aluminoxane. The non-solvent forces aromatic inclusion solvent (i.e., the aromatic solvent that is included in the clathrate structure or composition) out of the clathrate, and thus yields a new composition as solids which leads to formation of the precipitate. While various inert non-solvents can be used, preferred non-solvents for this use are liquid paraffinic and/or cycloparaffinic hydrocarbons, such as one or more liquid pentane, hexane, heptane, octane, nonane, or decane isomers, cyclopentane, one or more liquid alkylcyclopentanes, cyclohexane, one or more liquid alkylcyclohexanes, and any mixture of any two or more of such hydrocarbons. This treatment with a non-solvent can be conducted at ambient room temperatures or at suitably reduced or elevated temperatures, e.g., in the range of about 20 to about 80°C. The amount of non-solvent used should be an amount that produces a good yield of precipitated solids, and this is readily determined in any situation by adding the non-solvent in portions and observing whether a further addition results in more precipitate formation. The precipitated solids are then recovered, e.g., by filtration, centrifugation, decantation, or like techniques. Preferably the recovered solids are washed with fresh non-solvent. This entire procedure can then be repeated one or more times if desired by redissolving the solids in aromatic solvent, removing the upper washing solvent layer, mixing the clathrate with non-solvent, and recovering the precipitate. At the end of the process, regardless of whether the entire procedure was repeated and if so, how many times it was repeated, the solids constitute a new highly ionic aluminoxanate of this invention. Where the procedure is repeated, it is preferred to wash at least the final recovered solids with fresh non-solvent. The solids can then be dried and stored in a suitably inert environment and atmosphere.

[0033] The solids formed in the above process have a higher electrical conductivity than the solids precipitated from the initial clathrate by addition of a non-solvent under the same conditions, thus demonstrating their more distinct ionic character.

[0034] The ionic aluminoxanates of this invention can be used in the formation of supported and unsupported catalytic systems for the polymerization of olefins and/or other functional monomers which on polymerization result in formation of polymerized ethylene linkages. Typically unsupported catalysts are formed by mixing or otherwise interacting the ionic aluminoxanate of this invention with the transition metal catalyst compound in an inert aromatic solvent. The resultant unsupported reaction product, which is an active olefin polymerization catalyst, can be formed using various proportions of these components. For example, the molar ratio of aluminum to transition metal can be in the range of about 20:1 to about 2000:1, and preferably is in the range of about 20:1 to about 200:1.

[0035] The foregoing operations described herein are conducted under conventional inert atmospheres using suitably anhydrous materials.

[0036] Without being bound by theory, the available experimental evidence, especially proton and silicon NMR, clearly indicates that the chelated ionic aluminoxanates of this invention are composed of a complexed or coordinated  $AlR_2$  monovalent cation and a univalent anion composed of an aluminoxane moiety containing an extra leaving group such as an extra hydrocarbyl group. The complexing or coordinating entity of the cation is derived from the polyether, crown-ether, or polysiloxane compound used in forming the original clathrate from which the ionic aluminoxanate is formed. Note Fig. 1 for a depiction of one such compound. The net effect of the new aluminoxanate compositions may be considered as the separation of an aluminoxane into its effective or active components as a catalyst activator, namely cationic  $Me_2Al^+$  and anionic  $MAOMe^\ominus$  in the case of methylaluminoxane (MAO).

#### Supported Ionic Aluminoxanates and Catalysts of this Invention

[0037] Instead of isolating the ionic aluminoxanates of this invention as particulate solids, the ionic aluminoxanates can be deposited on a support. Various methods for preparing supported catalysts of this invention have been described hereinabove. In all cases, a catalytically-active catalyst composition is formed by interaction between an ionic aluminoxanate of this invention and one or more transition metal compounds of Groups 3 to 10 including the lanthanide series and the actinide series, and this catalyst composition is supported on the catalyst support or carrier used. One way of accomplishing this is to mix the transition metal compound(s) with a slurry of a supported ionic aluminoxanate of this invention. Another way is to mix an ionic aluminoxanate of this invention with a slurry of supported transition metal compound(s). Still another way is to premix an ionic aluminoxanate of this invention with the transition metal compound(s), and contact the resultant reaction product with a catalyst support or carrier. The operations are typically conducted in a suitable inert liquid phase such as in a liquid hydrocarbon diluent such as a liquid aromatic hydrocarbon. When the transition metal catalyst compound or complex is itself a liquid, the supported catalyst of this invention can be made for example by contacting or mixing the supported ionic aluminoxanate of this invention with the liquid transition metal catalyst compound or complex. Various ratios of supported ionic aluminoxanate of this invention to the liquid transition metal catalyst compound or complex can be used. For example these components can be proportioned such that the mole ratio of aluminum to transition metal is in the range of about 20:1 to about 2000:1, and preferably in the range of about 20:1 to about 200:1. Temperatures in the range of about 20 to about 80°C are typically used.

#### Self-Supported Catalysts of this Invention

[0038] Self-supported catalysts and methods for producing such self-supported catalysts are additional embodiments of this invention. A self-supported catalyst of this invention can be

formed by a process which comprises:

- I) mixing together components comprised of (A) at least one catalyst compound or complex of a transition metal including the lanthanide series and the actinide series, and (B) a viscous liquid composed of ionic aluminoxanate and included aromatic solvent; and
- II) recovering a self-supported catalyst from the mixture formed in I).

The viscous liquid of (B) is formed by a process which comprises thoroughly washing one or more times with an aromatic solvent, a liquid clathrate formed from (i) an aluminoxane, (ii) an effective amount of an organic, inorganic, or organometallic compound, and (iii) an aromatic organic solvent, each washing forming a two-phase system composed of a lower layer of a viscous liquid composed of ionic aluminoxanate and included aromatic solvent, and an upper layer of a less dense liquid, and each time removing and discarding the layer of less dense liquid such that a viscous liquid remains. Different procedures can be used in II) above for recovering the self-supported catalyst. Among ways of recovering the self-supported catalyst from the mixture formed in I) above is a procedure comprising (a) adding to or mixing with the mixture formed in I) a non-solvent to precipitate self-supported catalyst as solids, and recovering such solids by use of a physical solids/liquid separation procedure, or (b) by subjecting the mixture formed in I) to vacuum distillation to remove the included aromatic solvent from said mixture, or (c) by spray drying the solids or the mixture formed in I).

[0039] Another method of producing the self-supported catalysts of this invention is a method which comprises interacting components comprised of (A) at least one catalyst compound or complex of a transition metal including the lanthanide series and the actinide series, and (B) an ionic aluminoxanate of this invention, this interacting being conducted in an inert solvent or diluent such as an alkane or cycloalkane when (A) and (B) are solids. Such interaction is typically conducted at temperatures of up to about 50°C, and oftentimes at ambient room temperatures.

[0040] While any aluminoxanate of this invention may be used, preferred self-supported catalyst are produced as above using an aluminoxanate derived from a C<sub>1-6</sub> alkylaluminoxane. In other words, the parent aluminoxane is a preferably a C<sub>1-6</sub> alkylaluminoxane, and most preferably is methylaluminoxane.

[0041] To further illustrate one of the above methods for forming a self-supported catalyst composition of this invention, a metallocene or transition metal complex is brought into admixture with a washed liquid clathrate composition. Any upper layer is removed and the lower layer is optionally washed with more aromatic solvent. Thereafter, a non-solvent such as an aliphatic hydrocarbon is added to precipitate the self-supported catalyst composition which consists of the aluminoxanate and the metallocene. By non-solvent as used herein is

meant a liquid which will not dissolve the intended material. In this case, an aliphatic hydrocarbon is a typical example of a non-solvent.

[0042] The foregoing operations described herein are conducted under conventional inert atmospheres using suitably anhydrous materials.

#### Transition Metal Catalyst Compounds

[0043] The new ionic aluminoxanates are so effective as cocatalysts that they can be used with any known transition metal catalyst compound in which the transition metal thereof is a Group 3 to 11 (typically a Group 3 to 10) transition metal of the Periodic Table including compounds of a metal of the lanthanide or actinide series. The Periodic Table referred to herein is that appearing on page 27 of the February 4, 1985 issue of *Chemical & Engineering News*. Suitable catalyst compounds can also be described as d- and f- block metal compounds. See, for example, the Periodic Table appearing on page 225 of Moeller, et al., *Chemistry*, Second Edition, Academic Press, copyright 1984. As regards the metal constituent, preferred are compounds of Cu, Fe, Co, Ni, Pd, and V. More preferred are compounds of the metals of Groups 4-6 (Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, and W), and most preferred are the Group 4 metals, especially titanium, zirconium, or hafnium.

[0044] Thus the transition metal catalyst compounds used in this invention can be one or more of any Ziegler-Natta catalyst compound, any metallocene, any compound of constrained geometry, any late transition metal complex, or any other transition metal compound or complex reported in the literature or otherwise generally known in the art to be an effective catalyst compound when suitably activated, including mixtures of at least two different types of such transition metal compounds or complexes, such as for example a mixture of a metallocene and a Ziegler-Natta olefin polymerization catalyst compound.

[0045] Among the transition metal compounds of the metals of Groups 3, 4, 5, and 6 which can be used as the transition metal component of the catalyst compositions of and used in this invention are the compounds of such metals as scandium, titanium, zirconium, hafnium, cerium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, thorium and uranium often referred to as Ziegler-Natta type olefin polymerization catalysts. Preferred compounds of this type can be represented by the formula  $MX_n(OR)_m$  in which M represents the transition metal atom or a transition metal atom cation containing one or two oxygen atoms such as vanadyl, zirconyl, or uranyl, X represents a halogen atom, OR represents a hydrocarbyloxy group having up to about 18 carbon atoms, preferably up to about 8 carbon atoms, and more preferably alkyl of up to about 4 carbon atoms, such as an alkyl, cycloalkyl, cycloalkylalkyl, aryl, or aralkyl, group and n and m are positive integers except that either one of them (but not both) can be zero, and where  $n + m$  is the valence state of the transition metal. Illustrative of some of the transition metal compounds which can be used are, for example, titanium dibromide, titanium tribromide, titanium tetrabromide, titanium dichloride,



titanium trichloride, titanium tetrachloride, titanium trifluoride, titanium tetrafluoride, titanium diiodide, titanium triiodide, titanium tetraiodide, zirconium dibromide, zirconium tribromide, zirconium tetrabromide, zirconium dichloride, zirconium trichloride, zirconium tetrachloride, zirconium tetrafluoride, zirconium tetraiodide, hafnium tetrafluoride, hafnium tetrachloride, hafnium tetrabromide, hafnium tetraiodide, hafnium trichloride, hafnium tribromide, hafnium triiodide, vanadium dichloride, vanadium trichloride, vanadium tetrachloride, vanadium tetrabromide, vanadium tribromide, vanadium dibromide, vanadium trifluoride, vanadium tetrafluoride, vanadium pentafluoride, vanadium diiodide, vanadium triiodide, vanadium tetraiodide, vanadyl chloride, vanadyl bromide, niobium pentabromide, niobium pentachloride, niobium pentafluoride, tantalum pentabromide, tantalum pentachloride, tantalum pentafluoride, chromous bromide, chromic bromide, chromous chloride, chromic chloride, chromous fluoride, chromic fluoride, molybdenum dibromide, molybdenum tribromide, molybdenum tetrabromide, molybdenum dichloride, molybdenum trichloride, molybdenum tetrachloride, molybdenum pentachloride, molybdenum hexafluoride, lanthanum trichloride, cerous fluoride, cerous chloride, cerous bromide, cerous iodide, ceric fluoride, uranium trichloride, uranium tetrachloride, uranium tribromide, uranium tetrabromide, thorium tetrachloride, thorium tetrabromide, and the like. Among the hydrocarbyloxides and mixed halide/hydrocarbyloxides of the transition metals are  $\text{Ti}(\text{OCH}_3)_4$ ,  $\text{Ti}(\text{OCH}_3)\text{Cl}_3$ ,  $\text{Ti}(\text{OCH}_3)\text{Br}_3$ ,  $\text{Ti}(\text{OCH}_3)_2\text{I}_2$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)\text{Br}_3$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)\text{Br}_3$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)\text{I}_3$ ,  $\text{Ti}(\text{OC}_3\text{H}_7)_2\text{Cl}_2$ ,  $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_3\text{Cl}$ ,  $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_2\text{Cl}_2$ ,  $\text{Ti}(\text{O-iso-C}_3\text{H}_7)\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)_2\text{Cl}_2$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_6\text{H}_5)\text{Cl}_3$ ,  $\text{Ti}(\text{O-p-CH}_3\text{C}_6\text{H}_4)\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_6\text{H}_{13})_2\text{Cl}_2$ ,  $\text{Ti}(\text{OC}_6\text{H}_{13})\text{Cl}_3$ ,  $\text{Ti}(\text{O-cyclo-C}_6\text{H}_{11})\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_8\text{H}_{17})_2\text{Br}_2$ ,  $\text{Ti}(\text{O-2-EtHex})_4$ ,  $\text{Ti}(\text{OC}_{12}\text{H}_{25})\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_{17}\text{H}_{18})_2\text{Br}_2$ ,  $\text{Zr}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Zr}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Zr}(\text{OC}_5\text{H}_{11})_4$ ,  $\text{ZrCl}(\text{OC}_2\text{H}_5)_3$ ,  $\text{ZrCl}_2(\text{OC}_2\text{H}_5)_2$ ,  $\text{ZrCl}_3(\text{OC}_2\text{H}_5)$ ,  $\text{ZrCl}(\text{OC}_4\text{H}_9)_3$ ,  $\text{ZrCl}_2(\text{OC}_4\text{H}_9)_2$ ,  $\text{ZrCl}_3(\text{OC}_4\text{H}_9)$ ,  $\text{Hf}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Hf}(\text{OC}_4\text{H}_9)_3\text{Cl}$ ,  $\text{VO}(\text{OC}_2\text{H}_5)_3$ ,  $\text{VOCl}(\text{OCH}_3)_2$ ,  $\text{VOCl}(\text{OC}_2\text{H}_5)_2$ ,  $\text{VOCl}(\text{OC}_3\text{H}_7)_2$ ,  $\text{VOCl}(\text{O-iso-C}_3\text{H}_7)_2$ ,  $\text{VOCl}_2(\text{OCH}_3)$ ,  $\text{VOCl}_2(\text{OC}_2\text{H}_5)$ ,  $\text{VOCl}_2(\text{OC}_3\text{H}_7)$ ,  $\text{VOCl}_2(\text{O-iso-C}_3\text{H}_7)$ ,  $\text{VOBr}(\text{OCH}_3)_2$ ,  $\text{VOBr}(\text{OC}_2\text{H}_5)_2$ ,  $\text{VOBr}(\text{O-iso-C}_4\text{H}_9)_2$ ,  $\text{VOBr}_2(\text{OC}_3\text{H}_7)$ ,  $\text{VOBr}_2(\text{O-iso-C}_3\text{H}_7)$ ,  $\text{VOBr}_2(\text{OC}_4\text{H}_9)$ ,  $\text{VOBr}_2(\text{O-iso-C}_4\text{H}_9)$ ,  $\text{VOI}(\text{OCH}_3)_2$ ,  $\text{VOI}(\text{OC}_2\text{H}_5)_2$ ,  $\text{VOI}_2(\text{OCH}_3)$ ,  $\text{VOI}_2(\text{O-cyclo-C}_3\text{H}_5)$ ,  $\text{VOI}_2(\text{OC}_5\text{H}_{11})$ ,  $\text{VOI}_2(\text{O-cyclo-C}_6\text{H}_{11})$ ,  $\text{Cr}(\text{O-iso-C}_4\text{H}_9)_3$ ,  $\text{Mo}(\text{OC}_2\text{H}_5)_3$ , and the like. Carboxylic acid salts and various chelates of the transition metal can also be used but in general are less preferred. A few non-limiting examples of such salts and chelates include zirconyl acetate, uranyl butyrate, chromium acetate, chromium(III) oxy-2-ethylhexanoate, chromium(III) 2-ethylhexanoate, chromium(III) dichloroethylhexanoate, chromium(II) 2-ethylhexanoate, titanium(IV) 2-ethylhexanoate, bis(2,4-pentanedionate)titanium oxide, bis(2,4-pentanedionate)titanium dichloride, bis(2,4-pentanedionate)titanium dibutoxide, vanadyl acetylacetonate, chromium acetylacetonate, niobium acetylacetonate, zirconyl acetylacetonate, chromium octylacetoacetate, and the like.

Also, transition metal alkyls such as tetramethyl titanium, methyl titanium trichloride, tetraethyl zirconium, tetraphenyl titanium, and the like can be used.

[0046] Preferred transition metal compounds of the well-known Ziegler-Natta catalyst compounds are those of the Group 4 metals, including the alkoxides, halides, and mixed halide/alkoxide compounds. More preferred are  $\text{TiCl}_4$ ,  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$ , and  $\text{TiCl}_3$ , with  $\text{TiCl}_4$  being most preferred. Such more preferred compounds can be used in chelated form in order to facilitate solubility. Suitable chelated catalysts of this type are known and reported in the literature.

[0047] Metallocenes are another broad class of olefin polymerization catalyst compounds with which the ionic aluminoxanates of this invention can be used in forming novel highly effective catalysts of this invention. As used herein, the term "metallocene" includes metal derivatives which contain at least one cyclopentadienyl moiety. Suitable metallocenes are well known in the art and include the metallocenes of Groups 3, 4, 5, 6, lanthanide and actinide metals, for example, the metallocenes which are described in U.S. Pat. Nos. 2,864,843; 2,983,740; 4,665,046; 4,874,880; 4,892,851; 4,931,417; 4,952,713; 5,017,714; 5,026,798; 5,036,034; 5,064,802; 5,081,231; 5,145,819; 5,162,278; 5,245,019; 5,268,495; 5,276,208; 5,304,523; 5,324,800; 5,329,031; 5,329,033; 5,330,948; 5,347,025; 5,347,026; and 5,347,752, whose teachings with respect to such metallocenes are incorporated herein by reference.

[0048] Metallocene structures in this specification are to be interpreted broadly, and include structures containing 1, 2, 3 or 4 Cp or substituted Cp rings. Thus metallocenes suitable for use in this invention can be represented by Formula (I):



where Cp, independently in each occurrence, is a cyclopentadienyl-moiety-containing group which typically has in the range of 5 to about 24 carbon atoms; B is a bridging group or *ansa* group that links two Cp groups together or alternatively carries an alternate coordinating group such as alkylaminosilylalkyl, silylamido, alkoxy, siloxy, aminosilylalkyl, or analogous monodentate hetero atom electron donating groups; M is a d- or f-block metal atom; each X and each Y is, independently, a group that is bonded to the d- or f-block metal atom; a is 0 or 1; b is a whole integer from 1 to 3 (preferably 2); c is at least 2; d is 0 or 1. The sum of b, c, and d is sufficient to form a stable compound, and often is the coordination number of the d- or f-block metal atom.

[0049] Cp is, independently, a cyclopentadienyl, indenyl, fluorenyl or related group that can  $\delta$ -bond to the metal, or a hydrocarbyl-, halo-, halohydrocarbyl-, hydrocarbylmetalloid-, and/or halohydrocarbylmetalloid-substituted derivative thereof. Cp typically contains up to 75 non-hydrogen atoms. B, if present, is typically a silylene ( $-\text{SiR}_2-$ ), benzo ( $\text{C}_6\text{H}_4<$ ), substituted benzo, methylene ( $-\text{CH}_2-$ ), substituted methylene, ethylene ( $-\text{CH}_2\text{CH}_2-$ ), or substituted

ethylene bridge. M is preferably a metal atom of Groups 4-6, and most preferably is a Group 4 metal atom, especially hafnium, and most especially zirconium. X can be a divalent substituent such as an alkylidene group, a cyclometallated hydrocarbyl group, or any other divalent chelating ligand, two loci of which are singly bonded to M to form a cyclic moiety which includes M as a member. Each X, and if present Y, can be, independently in each occurrence, a halogen atom, a hydrocarbyl group (alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, aralkyl, *etc.*), hydrocarbyloxy, (alkoxy, aryloxy, *etc.*) siloxy, amino or substituted amino, hydride, acyloxy, triflate, and similar univalent groups that form stable metallocenes. The sum of b, c, and d is a whole number, and is often from 3-5. When M is a Group 4 metal or an actinide metal, and b is 2, the sum of c and d is 2, c being at least 1. When M is a Group 3 or Lanthanide metal, and b is 2, c is 1 and d is zero. When M is a Group 5 metal, and b is 2, the sum of c and d is 3, c being at least 2.

[0050] Also useful in this invention are compounds analogous to those of Formula (I) where one or more of the Cp groups are replaced by cyclic unsaturated charged groups isoelectronic with Cp, such as borabenzene or substituted borabenzene, azaborole or substituted azaborole, and various other isoelectronic Cp analogs. See for example Krishnamurti, et al., U.S. Pat. No. 5,554,775 and 5,756,611.

[0051] In one preferred group of metallocenes, b is 2, i.e., there are two cyclopentadienyl-moiety containing groups in the molecule, and these two groups can be the same or they can be different from each other.

[0052] Another sub-group of useful metallocenes which can be used in the practice of this invention are metallocenes of the type described in WO 98/32776 published July 30, 1998. These metallocenes are characterized in that one or more cyclopentadienyl groups in the metallocene are substituted by one or more polyatomic groups attached via a N, O, S, or P atom or by a carbon-to-carbon double bond. Examples of such substituents on the cyclopentadienyl ring include -OR, -SR, -NR<sub>2</sub>, -CH=, -CR=, and -PR<sub>2</sub>, where R can be the same or different and is a substituted or unsubstituted C<sub>1</sub>-C<sub>16</sub> hydrocarbyl group, a tri-C<sub>1</sub>-C<sub>8</sub> hydrocarbylsilyl group, a tri-C<sub>1</sub>-C<sub>8</sub> hydrocarbyloxysilyl group, a mixed C<sub>1</sub>-C<sub>8</sub> hydrocarbyl and C<sub>1</sub>-C<sub>8</sub> hydrocarbyloxysilyl group, a tri-C<sub>1</sub>-C<sub>8</sub> hydrocarbylgermyl group, a tri-C<sub>1</sub>-C<sub>8</sub> hydrocarbyloxygermyl group, or a mixed C<sub>1</sub>-C<sub>8</sub> hydrocarbyl and C<sub>1</sub>-C<sub>8</sub> hydrocarbyloxygermyl group.

[0053] Examples of metallocenes to which this invention is applicable include such compounds as:

bis(cyclopentadienyl)zirconium dimethyl;

bis(cyclopentadienyl)zirconium dichloride;

bis(cyclopentadienyl)zirconium monomethylmonochloride;

bis(cyclopentadienyl)titanium dichloride;

bis(cyclopentadienyl)titanium difluoride;  
 cyclopentadienylzirconium tri-(2-ethylhexanoate);  
 bis(cyclopentadienyl)zirconium hydrogen chloride;  
 bis(cyclopentadienyl)hafnium dichloride;  
 racemic and meso dimethylsilanylene-bis(methylcyclopentadienyl)hafnium dichloride;  
 racemic dimethylsilanylene-bis(indenyl)hafnium dichloride;  
 racemic ethylene-bis(indenyl)zirconium dichloride;  
 ( $\eta^5$ -indenyl)hafnium trichloride;  
 ( $\eta^5$ -C<sub>5</sub>Me<sub>3</sub>)hafnium trichloride;  
 racemic dimethylsilanylene-bis(indenyl)thorium dichloride;  
 racemic dimethylsilanylene-bis(4,7-dimethyl-1-indenyl)zirconium dichloride;  
 racemic dimethyl-silanylene-bis(indenyl)uranium dichloride;  
 racemic dimethylsilanylene-bis(2,3,5-trimethyl-1-cyclopentadienyl)zirconium dichloride;  
 racemic dimethyl-silanylene(3-methylcyclopentadienyl)hafnium dichloride;  
 racemic dimethylsilanylene-bis(1-(2-methyl-4-ethyl)indenyl) zirconium dichloride;  
 racemic dimethylsilanylene-bis(2-methyl-4,5,6,7-tetrahydro-1-indenyl) zirconium dichloride;  
 bis(pentamethylcyclopentadienyl)thorium dichloride;  
 bis(pentamethylcyclopentadienyl)uranium dichloride;  
 (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanetitanium dichloride;  
 (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane chromium dichloride;  
 (tert-butylamido)dimethyl(- $\eta^5$ -cyclopentadienyl)silanetitanium dichloride;  
 (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanemethyltitanium bromide;  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyluranium dichloride;  
 (tert-butylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium dichloride;  
 (methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediylcerium dichloride;  
 (methylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)-1,2-ethanediyltitanium dichloride;  
 (ethylamido)(tetramethyl- $\eta^5$ -cyclopentadienyl)methylenetitanium dichloride;  
 (tert-butylamido)dibenzyl(tetramethyl- $\eta^5$ -cyclopentadienyl)-silanebenzylvanadium chloride;  
 (benzylamido)dimethyl(indenyl)silanetitanium dichloride;  
 (phenylphosphido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silanebenzyltitanium chloride;  
 rac-dimethylsilylbis(2-methyl-1-indenyl)zirconium dimethyl;  
 rac-ethylenebis(1-indenyl)zirconium dimethyl;  
 bis(methylcyclopentadienyl)titanium dimethyl;  
 bis(methylcyclopentadienyl)zirconium dimethyl;  
 bis(n-butylcyclopentadienyl)zirconium dimethyl;  
 bis(dimethylcyclopentadienyl)zirconium dimethyl;  
 bis(diethylcyclopentadienyl)zirconium dimethyl;

bis(methyl-n-butylcyclopentadienyl)zirconium dimethyl;  
bis(n-propylcyclopentadienyl)zirconium dimethyl;  
bis(2-propylcyclopentadienyl)zirconium dimethyl;  
bis(methylethylcyclopentadienyl)zirconium dimethyl;  
bis(indenyl)zirconium dimethyl;  
bis(methylindenyl)zirconium dimethyl;  
dimethylsilylenebis(indenyl)zirconium dimethyl;  
dimethylsilylenebis(2-methylindenyl)zirconium dimethyl;  
dimethylsilylenebis(2-ethylindenyl)zirconium dimethyl;  
dimethylsilylenebis(2-methyl-4-phenylindenyl)zirconium dimethyl;  
1,2-ethylenebis(indenyl)zirconium dimethyl;  
1,2-ethylenebis(methylindenyl)zirconium dimethyl;  
2,2-propylidenebis(cyclopentadienyl)(fluorenyl)zirconium dimethyl;  
dimethylsilylenebis(6-phenylindenyl)zirconium dimethyl;  
bis(methylindenyl)zirconium benzyl methyl;  
ethylenebis[2-(tert-butyldimethylsiloxy)-1-indenyl] zirconium dimethyl;  
dimethylsilylenebis(indenyl)chlorozirconium methyl;  
5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene zirconium dimethyl;  
dimethylsilylenebis(2-methylindenyl)hafnium dimethyl;  
dimethylsilylenebis(2-ethylindenyl)hafnium dimethyl;  
dimethylsilylenebis(2-methyl-4-phenylindenyl)hafnium dimethyl;  
2,2-propylidenebis(cyclopentadienyl)(fluorenyl)hafnium dimethyl;  
bis(9-fluorenyl)(methyl)(vinyl)silane zirconium dimethyl,  
bis(9-fluorenyl)(methyl)(prop-2-enyl)silane zirconium dimethyl,  
bis(9-fluorenyl)(methyl)(but-3-enyl)silane zirconium dimethyl,  
bis(9-fluorenyl)(methyl)(hex-5-enyl)silane zirconium dimethyl,  
bis(9-fluorenyl)(methyl)(oct-7-enyl)silane zirconium dimethyl,  
(cyclopentadienyl)(1-allylindenyl) zirconium dimethyl,  
bis(1-allylindenyl)zirconium dimethyl,  
(9-(prop-2-enyl)fluorenyl)(cyclopentadienyl)zirconium dimethyl,  
(9-(prop-2-enyl)fluorenyl)(pentamethylcyclopentadienyl)zirconium dimethyl,  
bis(9-(prop-2-enyl)fluorenyl) zirconium dimethyl,  
(9-(cyclopent-2-enyl)fluorenyl)(cyclopentadienyl) zirconium dimethyl,  
bis(9-(cyclopent-2-enyl)(fluorenyl)zirconium dimethyl,  
5-(2-methylcyclopentadienyl)-5(9-fluorenyl)-1-hexene zirconium dimethyl,  
1-(9-fluorenyl)-1-(cyclopentadienyl)-1-(but-3-enyl)-1-(methyl)methane zirconium dimethyl,  
5-(fluorenyl)-5-(cyclopentadienyl)-1-hexene hafnium dimethyl,

(9-fluorenyl)(1-allylindenyl)dimethylsilane zirconium dimethyl,  
 1-(2,7-di(alpha-methylvinyl)(9-fluorenyl)-1-(cyclopentadienyl)-1,1-dimethylmethane  
 zirconium dimethyl,  
 1-(2,7-di(cyclohex-1-enyl)(9-fluorenyl))-1-(cyclopentadienyl)-1,1-methane zirconium  
 dimethyl,  
 5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene titanium dimethyl,  
 5-(cyclopentadienyl)-5-(9-fluorenyl)-1-hexene titanium dimethyl,  
 bis(9-fluorenyl)(methyl)(vinyl)silane titanium dimethyl,  
 bis(9-fluorenyl)(methyl)(prop-2-enyl)silane titanium dimethyl,  
 bis(9-fluorenyl)(methyl)(but-3-enyl)silane titanium dimethyl,  
 bis(9-fluorenyl)(methyl)(hex-5-enyl)silane titanium dimethyl,  
 bis(9-fluorenyl)(methyl)(oct-7-enyl)silane titanium dimethyl,  
 (cyclopentadienyl)(1-allylindenyl) titanium dimethyl,  
 bis(1-allylindenyl)titanium dimethyl,  
 (9-(prop-2-enyl)fluorenyl)(cyclopentadienyl)hafnium dimethyl,  
 (9-(prop-2-enyl)fluorenyl)(pentamethylcyclopentadienyl)hafnium dimethyl,  
 bis(9-(prop-2-enyl)fluorenyl) hafnium dimethyl,  
 (9-(cyclopent-2-enyl)fluorenyl)(cyclopentadienyl) hafnium dimethyl,  
 bis(9-(cyclopent-2-enyl)(fluorenyl)hafnium dimethyl,  
 5-(2-methylcyclopentadienyl)-5(9-fluorenyl)-1-hexene hafnium dimethyl,  
 5-(fluorenyl)-5-(cyclopentadienyl)-1-octene hafnium dimethyl,  
 (9-fluorenyl)(1-allylindenyl)dimethylsilane hafnium dimethyl.  
 (tert-butylamido)dimethyl(tetramethylcyclopentadienyl)silane titanium(1,3-pentadiene);  
 (cyclopentadienyl)(9-fluorenyl)diphenylmethane zirconium dimethyl;  
 (cyclopentadienyl)(9-fluorenyl)diphenylmethane hafnium dimethyl;  
 dimethylsilanylene-bis(indenyl) thorium dimethyl;  
 dimethylsilanylene-bis(4,7-dimethyl-1-indenyl) zirconium dimethyl;  
 dimethylsilanylene-bis(indenyl) uranium dimethyl;  
 dimethylsilanylene-bis(2-methyl-4-ethyl-1-indenyl) zirconium dimethyl;  
 dimethylsilanylene-bis(2-methyl-4,5,6,7-tetrahydro-1-indenyl) zirconium dimethyl;  
 (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane titanium dimethyl;  
 (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane chromium dimethyl;  
 (tert-butylamido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane titanium dimethyl;  
 (phenylphosphido)dimethyl(tetramethyl- $\eta^5$ -cyclopentadienyl)silane titanium dimethyl; and  
 [dimethylsilanediy]bis(indenyl)]scandium methyl.

In many cases the metallocenes such as referred to above will exist as racemic mixtures, but  
 pure enantiomeric forms or mixtures enriched in a given enantiomeric form can be used.

[0054] Other organometallic catalytic compounds with which the ionic aluminoxanates of this invention can be used in forming novel catalysts of this invention are the late transition metal catalyst described, for example, in U.S. Pat. Nos. 5,516,739 to Barborak, et al.; 5,561,216 to Barborak, et al.; 5,866,663 to Brookhart, et al; 5,880,241 to Brookhart, et al; and 6,114,483 to Coughlin, et al. Such catalysts are sometimes referred to herein collectively as "a Brookhart-type late transition metal catalyst compound or complex".

[0055] Other transition metal catalyst compounds and catalyst complexes that can be used in the practice of this invention include cationic nickel, palladium, iron, and cobalt complexes containing diimine and bisoxazoline ligands such as described in Johnson et al. WO 96/23010; palladium and nickel catalysts containing selected bidentate phosphorus-containing ligands such as described in EP 381,495; cationic  $\alpha$ -diimine-based nickel and palladium complexes such as described by Johnson et al. in *J. Am. Chem. Soc.*, **1995**, *117*, 6414, see also Brown et al. WO 97/17380; nickel complexes such as described by Johnson et al. in U.S. Pat. No. 5,714,556; cobalt(III) cyclopentadienyl catalytic systems such as described by Schmidt et al. in *J. Am. Chem. Soc.*, **1985**, *107*, 1443, and by Brookhart et al. in *Macromolecules*, **1995**, *28*, 5378; anionic phosphorus, oxygen donors ligated to nickel(II) such as described by Klabunde in U.S. Pat. Nos. 4,716,205, 4,906,754, 5,030,606, and 5,175,326; Group 8-10 transition metal complexes coordinated with a bidentate ligand such as described in WO 98/40374; transition metal complexes with bidentate ligands containing pyridine or quinoline moieties such as described in U.S. Pat. No. 5,637,660; quinolinoxy or pyridinoxy-substituted Group 4 transition metal trihalides such as described in U.S. Pat. No. 6,020,493; nickel complexes such as described by bis(ylide)nickel complexes such as described by Starzewski et al. in *Angew. Chem. Int. Ed. Engl.*, **1987**, *26*, 63, and U.S. Pat. No. 4,691,036; neutral N, O, P, or S donor ligands in combination with a nickel(O) compound and an acid such as described in WO 97/02298; aminobis(imino)phosphorane nickel catalysts such as described by Fink et al. in U.S. Pat. No. 4,724,273.

[0056] Illustrative, non-limiting additional examples of various types of transition metal compounds that can be employed include the following:

2,6-bis-[1-(1-methylphenylimino)ethyl]pyridine iron[II] chloride;

2,6-bis[1-(1-ethylphenylimino)ethyl]pyridine iron[II] chloride;

2,6-bis[1-(1-isopropylphenylimino)ethyl]pyridine iron[II] chloride;

2,6-bis-(1-(2-methylphenylimino)ethyl)pyridine iron(II) chloride;

N,N'-di(trimethylsilyl)benzamidinato copper(II);

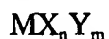
tridentate Schiff base complexes of cobalt and iron described by Mashima in *Shokubai* **1999**, vol. *41*, p. 58;

nickel compounds of the type described in U. S. Patent 5,880,323;

nickel(II) acetylacetonate;

bis(acetonitrile)dichloro palladium(II);  
 bis(acetonitrile)bis(tetrafluoroborate)palladium(II);  
 (2,2'-bipyridine)dichloro palladium(II);  
 bis(cyclooctadienyl) nickel(0);  
 palladium(II) acetylacetonate;  
 bis(salicylaldiminato) complexes of the type described by Matsui *et. al.* in *Chemistry Letters* 2000, pp. 554-555;  
 cobalt dioctoate;  
 cobaltocene;  
 (cyclopentadienyl)(triphenylphosphino)cobalt(II) diiodide; and  
 nickel compounds of the type described in JP 09-272709.

[0057] Preferred transition metal compounds which can be used in forming the catalysts of this invention are transition metal compounds which can be represented by the formula:



where M is a transition metal of Group 4 to 8 including the lanthanide series and actinide series, and preferably of Group 4 to 6, of the Periodic Table, and Y is, independently, a halide or pseudohalide, n is the valence of M, and m is an integer of from 0 to n-1. Of the pseudohalides, preferred are alkoxide or oxyhalide groups. Pseudohalides, which is a term of art, refers to anionic moieties which as salt-like anions which are non-halogenides. Non-limiting examples of suitable pseudohalide groups are oxyhalide groups, hydrocarbyloxy groups (-OR groups such as alkoxy, aryloxy, cycloalkoxy, arylalkoxy, etc.), amido groups (-NR<sub>2</sub>), hydrocarbylthio groups (-SR groups), and the like. Most preferred are compounds of the above formula wherein M is a Group 4 metal. Non-limiting examples of suitable transition metal compounds include, for example, transition metal halides and oxyhalides such as titanium dibromide, titanium tribromide, titanium tetrabromide, titanium dichloride, titanium trichloride, titanium tetrachloride, titanium trifluoride, titanium tetrafluoride, titanium diiodide, titanium tetraiodide, zirconium dibromide, zirconium tribromide, zirconium tetrabromide, zirconium dichloride, zirconium trichloride, zirconium tetrachloride, zirconium tetrafluoride, zirconium tetraiodide, hafnium tetrafluoride, hafnium tetrachloride, hafnium tetrabromide, hafnium tetraiodide, hafnium trichloride, hafnium tribromide, hafnium triiodide, hafnium oxychloride, vanadium dichloride, vanadium trichloride, vanadium tetrachloride, vanadium trifluoride, vanadium tetrafluoride, vanadium pentafluoride, vanadium triiodide, vanadium oxytrichloride, vanadium oxytribromide, niobium pentabromide, niobium pentachloride, niobium pentafluoride, tantalum pentabromide, tantalum pentachloride, tantalum pentafluoride, chromous bromide, chromic bromide, chromous chloride, chromic chloride, chromous fluoride, chromic fluoride, molybdenum dibromide, molybdenum tribromide, molybdenum tetrabromide, molybdenum dichloride,



molybdenum trichloride, molybdenum tetrachloride, molybdenum pentachloride, molybdenum hexafluoride, lanthanum trichloride, cerous fluoride, cerous chloride, cerous bromide, cerous iodide, ceric fluoride, uranium trichloride, uranium tetrachloride, uranium tribromide, uranium tetrabromide, thorium tetrachloride, thorium tetrabromide, and the like. Among suitable alkoxides and mixed halide/alkoxides of the transition metals are  $\text{Ti}(\text{OCH}_3)_4$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}$ ,  $\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl}_3$ ,  $\text{Ti}(\text{O-iso-C}_3\text{H}_7)\text{Cl}_3$ ,  $\text{Ti}(\text{OC}_4\text{H}_9)_3\text{Cl}$ ,  $\text{Ti}(\text{OC}_3\text{H}_7)_2\text{Cl}_2$ ,  $\text{Ti}(\text{O-iso-C}_3\text{H}_7)_2\text{Cl}_2$ ,  $\text{Ti}(\text{OC}_{17}\text{H}_{18})_2\text{Br}_2$ ,  $\text{Zr}(\text{OC}_2\text{H}_5)_4$ ,  $\text{Zr}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Zr}(\text{OC}_5\text{H}_{11})_4$ ,  $\text{ZrCl}_3(\text{OC}_2\text{H}_5)$ ,  $\text{ZrCl}(\text{OC}_4\text{H}_9)_3$ ,  $\text{Hf}(\text{OC}_4\text{H}_9)_4$ ,  $\text{Hf}(\text{OC}_4\text{H}_9)_3\text{Cl}$ ,  $\text{VO}(\text{OC}_2\text{H}_5)_3$ ,  $\text{Cr}(\text{O-iso-C}_4\text{H}_9)_3$ ,  $\text{Mo}(\text{OC}_2\text{H}_5)_3$ , and the like. Other transition metal compounds which may be used include amides such as  $\text{Ti}(\text{NMe}_2)_4$ ,  $\text{Zr}(\text{NMe}_2)_4$ ,  $\text{Ti}(\text{NEt}_2)_4$ ,  $\text{Zr}(\text{NEt}_2)_4$ , and  $\text{Ti}(\text{NBu}_2)_4$ ; carboxylic acid salts such as titanium oxalate, cobalt acetate, chromium acetate, nickel formate, thallium oxalate, and uranyl formate. Among the more preferred transition metal compounds are the halides, oxyhalides, alkoxides, and mixed halide-alkoxides of the Group 4 to 6 metals, and more particularly of the metals of Groups 4 and 5. Among especially preferred transition metal compounds are the trivalent or tetravalent Group 4 metal halides, particularly the chlorides, and the vanadium oxyhalides, particularly vanadium oxytrichloride. The Periodic Table referred to is that appearing on page 27 of the February 4, 1985 issue of *Chemical & Engineering News*.

[0058] Supported catalysts of this invention can be prepared by combining in any order the transition metal compound, an ionic aluminoxanate of this invention, and the support in one or more suitable solvents or diluent. Suitable solvents and/or diluents include, but are not necessarily limited to, straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane and the like; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcyclopentane and the like; and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene and the like. Mixtures of different types of such hydrocarbons can also be used, such as a mixture of one or more acyclic aliphatic hydrocarbons and one or more cycloaliphatic hydrocarbons; a mixture of one or more acyclic aliphatic hydrocarbons and one or more aromatic hydrocarbons; a mixture of one or more cycloaliphatic hydrocarbons and one or more aromatic hydrocarbons; or a mixture of one or more acyclic aliphatic hydrocarbons, one or more cycloaliphatic hydrocarbons, and one or more aromatic hydrocarbons.

[0059] It is preferred that the catalyst components as well as the resultant catalyst compositions be handled in an inert, moisture-free, oxygen free environment such as argon, nitrogen or helium because of the sensitivity of the catalyst components and catalyst compositions to moisture and oxygen.

[0060] In one method of forming the catalyst composition, the transition metal compound and an ionic aluminoxanate of this invention are combined in a first step in a suitable solvent

such as an aromatic solvent to produce a solution of the reaction product. This reaction may be carried out at one or more suitable temperatures within the range of about -100 to about 300°C, preferably about 0 to about 100°C. Holding times to allow for the completion of the reaction may range from about 10 seconds to about 60 minutes depending on the reaction variables. The solution produced by combining the transition metal compound and ionic aluminoxanate of this invention is then contacted with the support. The method of contact may vary, but it is preferred that the support be added to the catalyst solution with vigorous stirring. Again contact temperatures may range from about 0 to about 100°C depending upon the solvents used. Contact times may vary from about 10 seconds to about 60 minutes or longer. The solvent can then be removed, typically by applying a vacuum. The solution may or may not be heated in order to aid in the removal of the solvent.

[0061] A preferred method of forming the catalyst compositions of this invention comprises forming an ionic aluminoxanate of this invention in the presence of a porous catalyst support material, for example as a slurry in a suitable inert diluent; and contacting the resultant supported ionic aluminoxanate of this invention -- preferably after recovery and washing with an inert solvent or diluent -- with or in a solution of the transition metal compound in a suitable anhydrous inert solvent, preferably with agitation. In this way the ionic aluminoxanate and the transition metal compound can interact to produce an active supported catalyst composition.

[0062] Regardless of the method used in the preparation, the active supported catalyst can be recovered by evaporation of the solvent to obtain a free-flowing solid or alternatively, the active supported catalyst can be maintained in its slurry state for direct use. Another variant is to replace the original solvent/diluent with another inert liquid diluent such as a paraffinic hydrocarbon to thereby provide a slurry of active catalyst for use in the polymerization.

[0063] Modified supported catalysts of this invention can be prepared by combining in any order at least one transition metal compound, at least one ionic aluminoxanate of this invention, at least one modifier, and the support in one or more suitable solvents or diluents. A modifier may be defined as a compound containing a Lewis acid or basic functionality, such as, for example, tetraethoxysilane, phenyltri(ethoxy)silane, bis-tert-butylhydroxytoluene (BHT), N,N-dimethylaniline and the like. Suitable solvents and/or diluents are the same as those described above. It is preferred that these catalyst components be handled in an inert, moisture-free, oxygen-free environment such as argon, nitrogen or helium because of the sensitivity of the catalyst components to moisture and oxygen.

[0064] In a preferred method of forming a modified supported catalyst, the ionic aluminoxanate of this invention and the modifier are combined in a first step in a suitable solvent such as an aromatic solvent to produce a solution or slurry. The transition metal compound is then added to this solution. These combined steps may be carried out in the

temperature range of about -100 to about 300°C, and preferably in the range of about 0 to about 100°C. Holding times to allow for the completion of the reaction may range from about 10 seconds to about 60 minutes depending on the reaction variables. The solution produced by combining the transition metal compound, the ionic aluminoxanate of this invention, and the modifier can then be contacted with the support, or preferably the ionic aluminoxanate of this invention is in the presence of the support as formed and thus is supported on the inorganic catalyst support *ab initio*. This supported ionic aluminoxanate of this invention is then treated with the modifier and then with the transition metal compound in a suitable inert organic medium such as an aromatic solvent to produce a slurry of active modified catalyst of this invention. In these operations contact temperatures may range from about 0 to about 100°C depending upon the solvents used. Contact times may vary from about 10 seconds to about 60 minutes or longer.

[0065] Regardless of the method used in forming the modified catalyst, the solvent or diluent can be removed, typically by applying a vacuum, in order to isolate the catalyst. The solution may or may not be heated in order to aid in the removal of the solvent. Alternatively the active catalyst slurry, with some of the solvent/diluent stripped away if desired, can be used as a component in conducting the polymerization. Another variant is to replace the original solvent/diluent with another inert liquid diluent such as a paraffinic hydrocarbon to thereby provide a slurry of active catalyst for use in the polymerization.

[0066] In accordance with this invention, optimum results are generally obtained wherein the molar ratio of ionic aluminoxanate of this invention to transition metal compound is from about 1.1 to about 20,000:1, preferably from about 10:1 to about 1000:1, and the molar ratio of ionic aluminoxanate of this invention to modifier is from about 1:1 to about 20,000:1, preferably from about 10:1 to about 1000:1. The concentration of transition metal compound on the support is typically between 0.01 wt% to about 100 wt%, preferably about 0.1 wt% to about 20 wt% based upon the weight of the support.

#### Catalyst Support Materials

[0067] Catalyst support materials used in the practice of this invention may be any finely divided inorganic solid support, such as talc, clay, silica, alumina, silica-alumina, or mixtures thereof or a particulate resinous support material such as spheroidal, particulate, or finely-divided polyethylene, polyvinylchloride, polystyrene, or the like. Preferred support materials are inorganic particulate solid catalyst supports or carrier materials such as magnesium halides, or the like, and particularly inorganic oxides, aluminum silicates, or inorganic compositions containing inorganic oxides, such as kaolinite, attapulgite, montmorillonite, illite, bentonite, halloysite, and similar refractory clays. Inorganic oxides that may be employed either alone or in combination with silica, alumina, or silica-alumina are magnesia, titania, zirconia, and the like. The inorganic oxides may be dehydrated to remove water. If

desired, the residual surface hydroxyl groups in the inorganic solid porous support may be removed by additional heating or by reaction with chemical dehydrating agents such as lithium alkyl, silylchloride, aluminum alkyls, or preferably with an ionic aluminoxanate of this invention. Preferred catalyst supports include dehydrated inorganic oxide treated with an aluminum alkyl or an aluminoxane such as methylaluminoxane. A suitable support material of this type is silica or silica gel treated with an aluminum alkyl or an aluminoxane.

[0068] Particularly preferred as the support material is particulate silica, especially porous particulate silica.

[0069] The specific particle size, surface area and pore volume of the inorganic support material determine the amount of inorganic support material that is desirable to employ in preparing the catalyst compositions, as well as affecting the properties of polymers formed with the aid of the catalyst compositions. These properties are frequently taken into consideration in choosing an inorganic support material for use in a particular aspect of the invention. A suitable inorganic support such as silica typically will have a particle diameter in the range of 0.1 to 600 microns, preferably in the range of 0.3 to 100 microns; a surface area in the range of 50 to 1000 m<sup>2</sup>/g, preferably in the range of 100 to 500 m<sup>2</sup>/g; and a pore volume in the range of about 0.3 to 5.0 cc/g, preferably in the range of 0.5 to 3.5 cc/g. It is also desirable to employ supports with pore diameters in the range of about 50 to about 500 angstroms. To ensure its use in dehydrated form the support material may be heat treated at 100-1000°C for a period of 1-100 hours, preferably 3-24 hours. The treatment may be carried out in a vacuum or while purging with a dry inert gas such as nitrogen.

[0070] As an alternative, the support material may be chemically dehydrated. Chemical dehydration is accomplished by slurrying the support in an inert low boiling solvent such as, for example, heptane, in the presence of the dehydrating agent such as for example, triethylaluminum in a moisture and oxygen-free atmosphere.

[0071] The supported catalyst systems of this invention are useful in producing olefin polymers and especially ethylene polymers, propylene polymers, ethylene/ $\alpha$ -olefin copolymers, styrene polymers and copolymers and the like.

[0072] In conducting the polymerizations pursuant to this invention, the catalyst components can be used in solution or deposited on a solid support. When used in solution polymerization, the solvent can be, where applicable, a large excess quantity of the liquid olefinic monomer. Typically, however, an ancillary inert solvent, typically a liquid paraffinic or aromatic hydrocarbon solvent is used, such as heptane, isooctane, decane, toluene, xylene, ethylbenzene, mesitylene, or mixtures of liquid paraffinic hydrocarbons and/or liquid aromatic hydrocarbons.

[0073] Polymers can be produced pursuant to this invention by homopolymerization of olefins, typically 1-olefins (also known as  $\alpha$ -olefins) such as ethylene, propylene, 1-butene,

styrene, or copolymerization of two or more copolymerizable monomers, at least one of which is typically a 1-olefin. The other monomer(s) used in forming such copolymers can be one or more different 1-olefins and/or a diolefin, and/or an acetylenic monomer. Olefins that can be polymerized in the presence of the catalyst compositions of this invention include  $\alpha$ -olefins having 2 to 20 carbon atoms such as ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. Normally, the hydrocarbon monomers used, such as 1-olefins, diolefins and/or acetylene monomers, will contain up to about 10 carbon atoms per molecule. Preferred 1-olefin monomers for use in the process include ethylene, propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 1-hexene, and 1-octene. It is particularly preferred to use supported or unsupported catalysts of this invention in the polymerization of ethylene, or propylene, or ethylene and at least one C<sub>3</sub>-C<sub>8</sub> 1-olefin copolymerizable with ethylene. Typical diolefin monomers which can be used to form terpolymers with ethylene and propylene include butadiene, hexadiene, norbornadiene, and similar copolymerizable diene hydrocarbons. 1-Heptyne and 1-octyne are illustrative of suitable acetylenic monomers which can be used.

[0074] Often the monomer used is a 1-alkene monomer whereby a homopolymer is prepared. In other frequent cases a mixture of a 1-alkene monomer such as ethylene and at least one monomer copolymerizable therewith is used whereby a copolymer is produced.

[0075] Polymerization of ethylene or copolymerization with ethylene and an  $\alpha$ -olefin having 3 to 10 carbon atoms may be performed in either the gas or liquid phase (*e.g.*, in a solvent, such as toluene, or heptane). The polymerization can be conducted at conventional temperatures (*e.g.*, 0° to 120°C.) and pressures (*e.g.*, ambient to 50 kg/cm<sup>2</sup>) using conventional procedures as to molecular weight regulations and the like.

[0076] The heterogeneous catalysts of this invention can be used in polymerizations conducted as slurry processes or as gas phase processes. By "slurry" in this connection is meant that the particulate catalyst is used as a slurry or dispersion in a suitable liquid reaction medium which may be composed of one or more ancillary solvents (*e.g.*, liquid aliphatic or aromatic hydrocarbons, *etc.*) or an excess amount of liquid monomer to be polymerized in bulk. Generally speaking, these polymerizations are conducted at one or more temperatures in the range of about 0 to about 160°C and under atmospheric, subatmospheric, or superatmospheric conditions. Preferably polymerizations conducted in a liquid reaction medium containing a slurry or dispersion of a catalyst of this invention are conducted at temperatures in the range of about 40 to about 110°C. Typical liquid diluents for such processes include isobutane, pentane, isopentane, hexane, heptane, toluene, and like materials. Typically, when conducting gas phase polymerizations, superatmospheric pressures are used, and the reactions are conducted at temperatures in the range of about 50 to about 160°C.

These gas phase polymerizations can be performed in a stirred or fluidized bed of catalyst in a pressure vessel adapted to permit the separation of product particles from unreacted gases. Thermostated ethylene, comonomer, hydrogen and an inert diluent gas such as nitrogen can be introduced or recirculated to maintain the particles at the desired polymerization reaction temperature. An aluminum alkyl such as triethylaluminum may be added as a scavenger of water, oxygen and other impurities. In such cases the aluminum alkyl is preferably employed as a solution in a suitable dry liquid hydrocarbon solvent such as toluene or xylene. Concentrations of such solutions in the range of about  $5 \times 10^{-5}$  molar are conveniently used. But solutions of greater or lesser concentrations can be used, if desired. Polymer product can be withdrawn continuously or semi-continuously at a rate that maintains a constant product inventory in the reactor.

[0077] In general, the polymerizations and copolymerizations conducted pursuant to this invention are carried out using a catalytically effective amount of a novel catalyst composition of this invention, which amount may be varied depending upon such factors such as the type of polymerization being conducted, the polymerization conditions being used, and the type of reaction equipment in which the polymerization is being conducted. In many cases, the amount of the catalyst of this invention used will be such as to provide in the range of about 0.000001 to about 0.01 percent by weight of transition, lanthanide, or actinide metal based on the weight of the monomer(s) being polymerized.

[0078] After polymerization and deactivation of the catalyst in a conventional manner, the product polymer can be recovered from the polymerization reactor by any suitable means. When conducting the process with a slurry or dispersion of the catalyst in a liquid medium the product typically is recovered by a physical separation technique (*e.g.*, decantation, *etc.*). The recovered polymer is usually washed with one or more suitably volatile solvents to remove residual polymerization solvent or other impurities, and then dried, typically under reduced pressure with or without addition of heat. When conducting the process as a gas phase polymerization, the product after removal from the gas phase reactor is typically freed of residual monomer by means of a nitrogen purge, and may possibly be used without further catalyst deactivation or catalyst removal.

[0079] When preparing polymers pursuant to this invention conditions may be used for preparing unimodal or multimodal polymer types. For example, mixtures of catalysts of this invention formed from two or more different metallocenes having different propagation and termination rate constants for ethylene polymerizations can be used in preparing polymers having broad molecular weight distributions of the multimodal type.

[0080] New Clathrates of this Invention

[0081] As mentioned above, this invention provides a new type of stable clathrate which can be effectively used in forming new ionic aluminoxanates of this invention using the

processes described herein. These clathrates are compositions formed from (i) an aluminoxane, (ii) an aliphatic or crown polyether, and (iii) an aromatic solvent, wherein the combination of (i), (ii), and (iii) is effective to form a clathrate. Component (i) is preferably a hydrocarbylaluminoxane such as, for example, one or a mixture of alkylaluminoxanes, one or a mixture of cycloalkylaluminoxanes, one or a mixture of arylaluminoxanes, one or a mixture of aralkylaluminoxanes, or a mixture of two or more of these different hydrocarbylaluminoxanes. Alkylaluminoxanes ( $C_{1-8}$ ) are typically used. Lower alkyl ( $C_{1-6}$ ) alkylaluminoxanes are preferred. Methylaluminoxane is most preferred. Non-limiting examples of candidate aliphatic polyethers and crown ethers for use as component (ii) include such compounds as dimethoxyethane, diethoxyethane, 1-ethoxy-2-methoxyethane, dipropoxyethane, 1,2-dimethoxypropane, 1,3-dimethoxypropane, 1,2-dimethoxybutane, 2,3-dimethoxybutane, 1,3,5-trimethoxypentane, 18-crown-6 polyether, and analogs and homologs thereof. Aromatic solvents useful as component (iii) include benzene, toluene, xylenes, ethylbenzene, cumene, tetrahydronaphthalene, and other liquid similar aromatic hydrocarbon solvents, including mixtures such as BTX.

[0082] These clathrate-forming compounds are preferably added in excess relative to the amount that dissolves to form the clathrate with the extra amount being easily removed, if desired. About stoichiometric or lesser amounts are effective to form stable clathrates, depending upon the aliphatic polyether or crown polyether used. Preferably, amounts of from about 0.01 to 0.5 moles of such polyether per mole of aluminum in the aluminoxane composition are added and more preferably from about 0.05 to 0.2 moles. The starting concentration of aluminoxane in solvent usually ranges from about 5 to 30 weight percent solution. As described herein, the weight percent of aluminoxane in the solutions is based on the total weight of aluminoxane and any unreacted trialkylaluminum in the solution.

[0083] The reaction temperature is chosen to provide a stable, liquid clathrate. By a stable liquid clathrate as used herein is meant that the two immiscible liquid layer systems remain intact such that the upper solvent layer can be separated from the lower clathrate layer. Although the use of ambient temperatures is most convenient (i.e. from about 15 to 30°C), some compounds require elevated temperatures of up to 80°C or higher in order to form a stable, liquid clathrate. A suitable temperature for any particular compound can be experimentally determined.

[0084] Removal of solvent from the dense lower liquid clathrate layer such as by vacuum distillation or the addition of excess non-aromatic solvent results in the isolation of solid, particulate compositions. The solid, particulate compositions are virtually insoluble in aliphatic hydrocarbons. When introduced into aromatic solvents, the novel solid composition will incorporate as much solvent as required to reform a liquid clathrate (inclusion solvent) which clathrate separates out from the rest of the solvent resulting again in two immiscible

liquid layers.

[0085] Besides being useful as starting materials for producing ionic aluminoxanates of this invention, the clathrates formed from (i) an aluminoxane, (ii) an aliphatic or crown polyether, and (iii) an aromatic solvent can be used in combination with metallocenes and/or transition metal compounds to provide olefin polymerization catalysts. The solid aluminoxanate composition remaining after removing the solvent from the dense lower liquid layer of these new clathrates, such as by vacuum distillation or the addition of excess non-aromatic solvent, likewise can be used in combination with metallocenes and/or transition metal compounds to provide olefin polymerization catalysts.

[0086] The following examples are presented for purposes of illustration, and are not intended to impose limitations on the scope of this invention.

### EXAMPLE 1

#### Preparation of Solid Ionic Potassium Aluminoxanate

[0087] A solution of MAO in toluene (60g, 307.4 mmol Al) was treated with KCl (2.3g, 30.84 mmol). The mixture was stirred at room temperature overnight. Liquid clathrate formation was observed and practically all solid KCl dissolved. Then the upper solution phase was separated by decantation. The lower viscous layer was washed with toluene (3 x 100mL). In order to obtain a solid ionic potassium aluminoxanate product, at this stage, cyclohexane was used to further wash the viscous oil until solid precipitate was formed. Then the slurry was filtered and washed with cyclohexane.

### EXAMPLE 2

#### Preparation of Silica-Supported Potassium Aluminoxanate

[0088] A solution of MAO in toluene (60g) and KCl (2.3g) were allowed to react as described in Example 1. The resulting viscous lower layer was washed with toluene, and then treated with silica (60g). A dry solid product was obtained. Enough cyclohexane was then added to the solid product to ensure easy stirring. The stirred slurry was then heated at 80°C for two hours. The slurry was filtered and the solid residue was washed with cyclohexane (3 x 50 mL). The solid product was then dried under reduced pressure at 60°C for 6 hours to obtain 74g of free-flowing potassium aluminoxanate supported on silica.

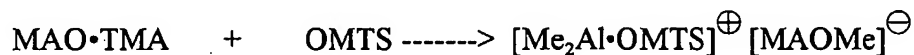
### EXAMPLE 3

#### Preparation and Characterization of a Siloxane-Complexed Dimethylaluminum Methylaluminoxanate (DMAM.OMTS)

[0089] A 30% solution of MAO in toluene (60g, 308 mmol Al) was treated octamethyltrisiloxane (OMTS, 3.65g, 15.4 mmol) at room temperature (RT). Clathrate



formation occurred. The mixture was stirred at RT overnight. The upper layer was removed by decantation. Then the lower layer was washed with toluene (3 x 100 mL). After each washing process, the lower layer became thicker. After the third wash, cyclohexane was added (2 x 100 mL) to precipitate the solid DMAM complex with OMTS (DMAM•OMTS). This solid product was filtered and washed with cyclohexane. After this thorough washing and precipitation as described above, the product was subjected to spectroscopic characterization. It was found that this product was a siloxane-complexed dimethylaluminum salt of methylaluminoxane [(Me<sub>2</sub>Al•OMTS)<sup>⊕</sup>(MAOMe)<sup>⊖</sup>] (which may also be termed a dimethylaluminum salt of a complexed methylaluminoxane). A representation of this product is set forth in Figure 1. The proton NMR of this product, which is presented in Figure 2, clearly shows the presence of two methyl groups on aluminum (Me<sub>2</sub>Al)<sup>⊕</sup> by comparative integration of OMTS peaks [(6:2):2].



This product showed two unusual downfield chemical shifts in <sup>29</sup>Si NMR, depicted in Figure 3, at 29 and 39 ppm with respect to Me<sub>4</sub>Si as reference. Theoretical calculations by Professor J.A. Tossell of the University of Maryland have shown that the experimental silicon NMR chemical shifts are perfectly matched for [Me<sub>2</sub>Al•OMTS]<sup>⊕</sup> composition. It will be noted that the cation contains dimethylaluminum moiety coordinated with an OMTS ligand.

[0090] While the composition of DMAM is ultimately derived from a conventional methylaluminoxane composition (MAO), a significant difference in their chemical composition is clearly illustrated by NMR spectroscopies and conductivity measurements. Proton NMR (Figure 2) and <sup>27</sup>Al NMR (Figure 4) clearly indicate the difference in chemical compositions of these two materials.

#### EXAMPLE 4

[0091] Comparative experiments were conducted demonstrating the changes that occur in electrical conductivity resulting from treatment of clathrates in accordance with processes of this invention. In these experiments 8 different compositions in the form of solids were dissolved in methylene chloride at a concentration of 1.67 wt%. A control sample of MAO at the same concentration in toluene was also formed. The electrical conductivity of each of the 8 test solutions at room temperature was determined by use of a VWR Digital Conductivity Meter. The solids tested were as follows:

- 1) MAO (in toluene) was formed by removing the toluene from a commercial 30 wt% solution of MAO in toluene, and dissolving a portion of the resultant solids in fresh

toluene to the specified test concentration.

- 2) MAO (in methylene chloride) was formed by dissolving MAO solids formed as in 1) in methylene chloride to the specified test concentration. After conductivity measurement this compound was promptly discarded because of the unpredictable reactivity of MAO with  $\text{CH}_2\text{Cl}_2$ .
- 3) Stabilized MAO was formed by mixing 2 mole % of octamethyltrisiloxane with a 30% solution of MAO in toluene, and then removing the toluene solvent to form solids. The solids were then dissolved in methylene chloride to the specified test concentration.
- 4) Washed DMAM (2) was formed by adding additional toluene to the initial solution formed in 3) above. This resulted in formation of a clathrate as a separate lower oily layer. After removing the upper layer, the lower clathrate layer was treated with heptane whereby solids precipitated. These solids were dissolved in methylene chloride to the specified test concentration.
- 5) Unwashed DMAM (5) was formed by mixing 5 mole % of octamethyltrisiloxane with a 30% solution of MAO in toluene. A clathrate was formed and the upper liquid layer was decanted away from the lower oily clathrate layer. The residual oily clathrate material was then treated with cyclohexane whereby solids precipitated. These solids were recovered and dissolved in methylene chloride to the specified test concentration.
- 6) Washed DMAM (5) was formed by thoroughly washing the initial clathrate product formed as in 5) above with toluene and precipitating the DMAM solids by addition of cyclohexane to the solution. These washed DMAM solids of this invention were then recovered and dissolved in methylene chloride to the specified test concentration.
- 7) Unwashed DMAM•DME (5), was formed by mixing dimethoxyethane with a 30% solution of MAO in toluene whereby a new clathrate of this invention was formed. The upper organic layer was decanted away from the lower oily clathrate layer. The clathrate was then treated with cyclohexane to precipitate the unwashed DMAM•DME (5). In this DMAM the dimethylaluminum moiety is complexed with a dimethoxyethane ligand, and thus even though not washed, is a composition of this invention. This precipitated product was recovered and dissolved in methylene chloride to the specified test concentration.
- 8) Washed DMAM•DME (5) was formed by thoroughly washing the initial clathrate product formed as in 7) above in toluene and then precipitating the solid DMAM•DME by addition of cyclohexane to the lower oily clathrate layer. As in 7) the dimethylaluminum moiety of this DMAM is complexed with a dimethoxyethane ligand. These washed solids of this invention were recovered and dissolved in

methylene chloride to the specified test concentration.

- 9) Washed DMAM•15-CE-5 was formed by treating MAO solution with 15-crown ether. The resulting clathrate product was washed with toluene and then precipitated by addition of cyclohexane.

[0092] The results of these conductivity tests in which the conductivities of the respective solutions are expressed in micro-mhos, are summarized in the Table 1.

**TABLE 1**

<b>Composition</b>	<b>Conductivity</b>
MAO (in toluene), control	0
MAO (in methylene chloride), comparative	4
Stabilized MAO, comparative	66
Washed DMAM•OMTS (2), a composition of this invention	94
Unwashed DMAM•OMTS (5), a composition of this invention	96
Washed DMAM•OMTS (5), a composition of this invention	140
Unwashed DMAM•DME (5), a composition of this invention	123
Washed DMAM•DME (5), a composition of this invention	163
Washed DMAM•15-CE-5, a composition of this invention	129

[0093] It can be seen from the results in Table 1 that the compositions of this invention had significantly higher conductivities than the compositions not of this invention. It can also be seen that when the ionic methylaluminoxane was made from a clathrate formed from an aluminoxane, a polyether, and an aromatic solvent -- in this case methylaluminoxane, dimethoxyethane and toluene -- the ionic methylaluminoxane was highly conductive and thus highly ionic even before washing (123 micro-mhos). Indeed such unwashed ionic methylaluminoxane was more conductive than any of the comparative compositions not of this invention. Without desiring to be bound by theory, it is deemed possible that coordination of the dimethylaluminoxane moiety by the aliphatic polyether ligand may enhance the ionic character of the compound.

[0094] Examples 5-9 describe in greater detail the methods used to form some of the compositions tested in Example 4.

#### **EXAMPLE 5**

[0095] MAO solution in toluene (60g, 308 mmol Al) was treated with OMTS (3.65g, 15.4 mmol) at room temperature (RT). Clathrate formation was observed. The mixture was stirred at RT overnight. The upper layer was removed by decantation. Then the lower layer

was washed with toluene (3 x 100 ml). After each washing process, the lower layer became thicker. Then add cyclohexane (2 x 100ml) to precipitate the solid DMAM•OMTS. The solid product was filtered and washed with cyclohexane.

#### EXAMPLE 6

[0096] MAO solution (60g, 308 mmol Al) and OMTS (3.65g, 15.4 mmol) were allowed to interact as described in Example 6. The resulting clathrate composition was not washed with toluene. Cyclohexane was added to precipitate the solid DMAM•OMTS composition.

#### EXAMPLE 7

[0097] MAO solution in toluene (54.7g, 281.2 mmol) was treated with dimethoxyethane (DME, 1.27g, 14.06 mmol) at RT. Clathrate formation was immediately observed. The mixture was stirred at RT overnight. The clathrate mixture was heated at 90°C for 4 hours and a clear one layer solution resulted. On cooling to room temperature, the clathrate composition was reformed (2 immiscible liquid layers). The upper layer was removed by decantation. Then the lower layer was washed with toluene (3 x 100ml). The upper toluene layer was removed by decantation, and the viscous lower layer was treated with cyclohexane to obtain a solid slurry. The solid was removed by filtration and then washed with cyclohexane. The solid product was dried at reduced pressure to obtain free flowing solid dimethoxyethane complexed dimethylaluminum salt of methylaluminoxane (DMAM•DME).

#### EXAMPLE 8

[0098] MAO solution in toluene (54.7g, 281.2 mmol) was treated with DME (1.27g, 14.06 mmol) as described in example 8. The resulting liquid clathrate composition was not washed with toluene. But was precipitated by addition of cyclohexane as described above. The solid product, unwashed DMAM•DME was vacuum dried.

#### EXAMPLE 9

[0099] Surprisingly, we also found that cyclic crown ethers (CE) also react with MAO solution in toluene to give liquid clathrate compositions. After thorough washings of the clathrate solution and precipitation by cyclohexane addition, solid dimethylaluminum salts of MAO are obtained as crown ether complexes, DMAM•CE. Thus, treatment of MAO solution (20.9g, 107.4 mmol Al) with 15-CE-5 (1.18g, 5.37 mmol) immediately resulted in liquid clathrate formation. More toluene (60g) was added. Then the mixture stirred at RT overnight. The clathrate composition was heated at 90°C for two hours. On cooling, the clathrate composition was washed with toluene (3 x 50ml). The upper toluene layer was decanted. Solid dimethylaluminum salt of MAO was obtained as crown ether complex,

DMAM•15-CE-5, by precipitation with cyclohexane.

[0100] US Pat. No. 5,922,631 shows that addition of octamethyltrisiloxane (OMTS) at two mole percent or less resulted in the formation of stabilized MAO composition without the formation of liquid clathrate. Example 10 shows that the addition of 1,2-dimethoxyethane at two mole percent or less did not result in the formation of liquid clathrate, but gave a stabilized MAO solution.

#### EXAMPLE 10

[0101] MAO solution (94.8g, 487.3 mmol Al) was treated with DME (0.88g, 9.75 mmol, 2 mole% addition). No clathrate formation was observed. The mixture was stirred at RT overnight. Still no clathrate formed. Then the mixture was heated at 90°C for 4 hours. On cooling to room temperature, no clathrate formed. However, the solution product remained clear and colorless without any visible solid precipitate even after three months.

#### EXAMPLE 11

[0102] MAO solution in toluene (20.5g, 105.4 mmol Al) was treated with 18-CE-6 (1.4g, 5.26 mmol) and immediately a liquid clathrate composition formed. The lower layer was very thick. Therefore, more toluene (60g) was added. The reaction was carried out as described in Example 7. Solid dimethylaluminum salt of MAO was obtained as a crown ether complex, DMAM•18CE6 by precipitation with cyclohexane. The slurry was filtered and the solid product washed with cyclohexane and then vacuum dried.

[0103] A comparison of some of the distinguishing physical and chemical characteristics of the compositions of this invention as compared to the parent alkylaluminoxanes from which they are prepared, is presented in Table 2 in which the comparison is between DMAM and MAO.

TABLE 2

Properties	MAO	DMAM
Solubility in toluene	Yes	No (forms clathrate)
TMA content (by NMR)	>20 mole % Al	< 2 mole % Al
Reactivity with CH <sub>2</sub> Cl <sub>2</sub>	Violent	None
Distinct Me <sub>2</sub> Al <sup>⊕</sup> peak ( <sup>1</sup> H NMR)	No	Yes
<sup>27</sup> Al NMR aluminoxane peak	Broad, buried in baseline	Distinct peak centered at about -20 ppm
Potential reduction of catalyst center	High	Low
Storage stability as liquid	Precipitate/gel formation	Viscous but gel-free
Pyrophoricity of solid	Highly pyrophoric	Non-pyrophoric
Ionic salt composition/conductivity in CH <sub>2</sub> Cl <sub>2</sub>	No	Yes

[0104] Examples 12-14 describe formation of supported chelated ionic aluminoxanates of this invention.

#### EXAMPLE 12

##### *DMAM•DME Supported on Silica*

[0105] Thus, DMAM•DME prepared from MAO solution (54.7g, 281.2 mmol Al) and DME (1.27g, 14.06 mmol) as described in Example 8. After the liquid clathrate product had been washed, it was treated with silica (50g). More toluene (100 ml) was added to form a stirrable slurry. The slurry was heated at 90°C for two hours. On cooling, the slurry was filtered. The solid product was washed with toluene (2 x 50 ml) and cyclohexane (2 x 50 ml). The solid product was then vacuum dried.

[0106] Supported DMAM•15-CE-5, and supported DMAM•18-CE-6 can be formed in the same general manner as in Example 12.

#### EXAMPLE 13

##### *Silica Supported DMAM•OMTS*

[0107] Solid DMAM•OMTS product from Example 3 (3g) was treated with silica (6g) in chlorobenzene (40 ml). The mixture was stirred at room temperature for two hours. The colorless slurry was filtered and the solid residue was washed with toluene (4 x 5 ml) and then with cyclohexane (2 x 5 ml). The solid product DMAM/SIL was vacuum dried to give a free flowing solid product (8.7g).

#### EXAMPLE 14

##### *Catalyst Supported on DMAM•OMTS*

[0108] Solid DMAM.OMTS product from Example 3 (5g) was treated with zirconocene dichloride (0.1g) in toluene (40 mL). Intensely colored liquid clathrate resulted. The less colored upper layer was removed. The lower layer was washed with toluene (20 mL). Then cyclohexane was added to obtain solid catalyst composition supported on DMAM•OMTS.

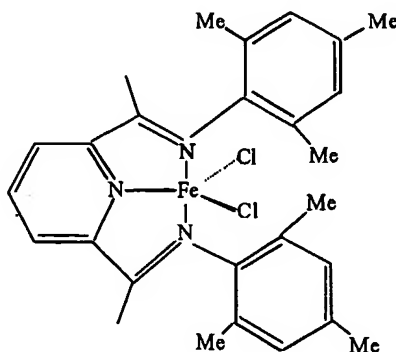
#### EXAMPLE 15

##### *Silica Supported Catalyst*

[0109] Silica supported DMAM product from example 13 (2g) was treated with zirconocene dichloride (0.05g) in toluene (40 mL). The slurry was stirred at room temperature for one hour. The slurry was filtered and washed with toluene (2 x 10 mL) and then with cyclohexane (2 x 10 mL). The solid product was vacuum dried.

**EXAMPLE 16****Ethylene Polymerization Runs with a Silica-Supported Iron Catalyst**

[0110] Comparative polymerizations were carried out at both 60 and 80°C in which ethylene was polymerized with the iron complex:



In one pair of runs, the supported catalyst was formed by contacting the iron complex with silica that had been pretreated with MAO as the cocatalyst or activator. In another pair of runs conducted under the same conditions using an equivalent metal content, the supported catalyst was formed by contacting the iron complex with silica that had been pretreated with DMAM as the cocatalyst or activator. The results of these comparative polymerizations are depicted graphically in Fig. 6. It can be seen from Fig. 6 that the ethylene consumption was substantially higher when conducting the polymerization pursuant to this invention using the supported catalyst of this invention in which DMAM was used as the cocatalyst or activator.

[0111] A number of additional clathrates suitable for use in forming ionic aluminoxanates of this invention were prepared as described in the above Examples and in U.S. Pat. No. 5,670,682 or 5,922,631. These clathrates were formed in each case from a 30 wt% solution of methylaluminumoxane in toluene (Albemarle Corporation). The compounds reacted therewith to form the clathrates were as follows: BuLi, KF, NaCl, LiF, KH, NaF, NaB(Ph)<sub>4</sub>, KOSiMe<sub>3</sub>, Ph<sub>3</sub>P=O, Ph<sub>3</sub>MePBr, Ph<sub>4</sub>PBr, 18-Crown-6, Et<sub>4</sub>NBF<sub>4</sub>, Me<sub>4</sub>NCl, iBu<sub>2</sub>NHHCl, iPr<sub>2</sub>NHHCl, and Ph<sub>3</sub>C<sup>⊕</sup> B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>⊖</sup>. A number of other compounds failed to form useful clathrates thus illustrating the unpredictability of such clathrate formation.

[0112] In addition to catalyst compounds of Groups 3 to 10 of the Periodic Table, this invention is also applicable to transition metal catalyst compounds of copper. Such copper compounds have been reported in the art to be effective as catalysts for the polymerization of olefins.

[0113] It is to be understood that the reactants and components referred to by chemical name or formula anywhere in this document, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another reactant, a solvent, or *etc.*). It matters not what preliminary chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical operation or reaction or in forming a mixture to be used in conducting a desired operation or reaction. Also, even though an embodiment may refer to substances, components and/or ingredients in the present tense ("is comprised of", "comprises", "is", *etc.*), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure.

[0114] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.



**CLAIMS:**

1. An ionic aluminoxanate which is electrically conductive when dissolved in methylene chloride.

2. An aluminoxanate as in Claim 1 wherein the electrical conductivity at 25°C of said ionic aluminoxanate if and when dissolved to a concentration of 1.67 weight percent in 99.9% A.C.S. HPLC grade, or better, methylene chloride, is at least 90 micro-mhos.

3. An aluminoxanate as in Claims 1 or 2 in which of the total aluminum in said aluminoxanate, and if any aluminum trialkyl is present therein, the amount of aluminum as aluminum trialkyl is less than 5 mole % as determined by proton NMR.

4. A method of producing an ionic aluminoxanate, which method comprises:

- A) thoroughly washing one or more times with an aromatic solvent, a liquid clathrate formed from (i) an aluminoxane, (ii) an effective amount of an organic, inorganic, or organometallic compound, and (iii) an aromatic organic solvent, each washing forming a two-phase system composed of a lower layer of a viscous liquid composed of ionic aluminoxanate and included aromatic solvent, and an upper layer of a less dense liquid, and (1) each time the layer of less dense liquid is removed and discarded such that a viscous liquid remains, or (2) when two or more washes are conducted, each time except for the last time the layer of less dense liquid is removed and discarded such that after the last time a two-phase liquid system remains; and
- B) recovering ionic aluminoxanate solids from the viscous liquid.

5. A method as in Claim 4 wherein said ionic aluminoxanate solids are recovered in B) by mixing a liquid non-solvent with said viscous liquid to precipitate said solids, and isolating the resultant solids.

6. A method as in Claim 5 wherein the resultant solids are isolated by use of a liquid/solids separation procedure.

7. A method as in Claim 5 wherein the resultant solids are isolated by spray drying said viscous liquid.

8. A method as in Claim 4 wherein said ionic aluminoxanate solids are recovered in B) by subjecting the viscous liquid remaining from (1) to vacuum distillation to remove the included aromatic solvent therefrom; or by subjecting the less dense liquid and the included aromatic solvent remaining from (2) to vacuum distillation to remove the less dense liquid and the included aromatic solvent therefrom.

9. A method of producing an ionic aluminoxanate, which method comprises:

- A) thoroughly washing a liquid clathrate formed from (i) an aluminoxane, (ii) an effective amount of an organic, inorganic, or organometallic compound, and (iii) an aromatic solvent, to form a viscous liquid clathrate;
- B) mixing an inert liquid non-solvent with viscous liquid clathrate from A) to form a

slurry comprised of precipitated particulate solids and a liquid phase; and

- C) recovering from the liquid phase precipitated particulate solids of said ionic aluminoxanate.

10. A method as in Claim 9 wherein the non-solvent is a liquid paraffinic or cycloparaffinic hydrocarbon.

11. A method of producing an ionic aluminoxanate, which method comprises:

- A) thoroughly washing a liquid clathrate formed from (i) an aluminoxane, (ii) an effective amount of an organic, inorganic, or organometallic compound, and (iii) an aromatic solvent, to form a product comprised of a liquid clathrate and solvent; and  
B) removing said solvent from liquid clathrate of A) by vacuum distillation to isolate particulate solids of said ionic aluminoxanate.

12. A method as in any of Claims 9-11 wherein the amount of washing in A) thereof is sufficient to form ionic aluminoxanate solids in which the electrical conductivity at 25°C of said ionic aluminoxanate if and when dissolved to a concentration of 1.67 weight percent in 99.9% A.C.S. HPLC grade, or better, methylene chloride, is higher than the electrical conductivity, under the same conditions, of the aluminoxane of A) (i) from which the ionic aluminoxanate is derived.

13. A method as in any of Claims 9-11 wherein the electrical conductivity at 25°C of said ionic aluminoxanate solids if and when dissolved to a concentration of 1.67 weight percent in 99.9% A.C.S. HPLC grade, or better, methylene chloride, is at least 90 micro-mhos.

14. A method as in any of Claims 9-13 wherein the amount of washing in A) thereof is sufficient to form ionic aluminoxanate solids in which if any aluminum trialkyl is present therein, the amount of aluminum as aluminum trialkyl relative to the total aluminum in said aluminoxanate, is less than 5 mole % as determined by proton NMR.

15. A method as in any of Claims 9-14 wherein (ii) thereof is an inorganic compound.

16. A method as in any of Claims 9-14 wherein (ii) thereof is (1) a monosiloxane, (2) a disiloxane in which the silicon atoms are separated from each other by an oxygen atom, or (3) a polysiloxane having at least 3 silicon atoms in the molecule and which are separated from each other by an oxygen atom such that there is a linear, branched or cyclic backbone of alternating Si and oxygen atoms, the remaining univalent bonds of the silicon atoms not interposed between oxygen atoms being individually satisfied by a univalent hydrocarbyl group.

17. A method as in Claim 16 wherein (ii) is a polysiloxane in which the univalent hydrocarbyl groups are, independently, methyl, ethyl, phenyl, or mixtures of any two or all three thereof.

18. A method as in Claim 16 wherein the polysiloxane used in forming said clathrate is octamethyltrisiloxane.
19. A method as in any of Claims 9-14 wherein (ii) thereof is an ether.
20. A method as in Claim 19 wherein the ether is an aliphatic polyether.
21. A method as in Claim 20 wherein the aliphatic polyether is a dialkoxyp propane or a dialkoxybutane.
22. A method as in Claim 21 wherein the aliphatic polyether is a 1,2-dialkoxymethane.
23. A method as in Claim 22 wherein the 1,2-dialkoxymethane is 1,2-dimethoxymethane.
24. A method as in any of Claims 9-14 wherein (ii) thereof is a crown-ether.
25. A method as in any of Claims 9-24 wherein (i) thereof is a hydrocarbylaluminumoxane.
26. A method as in Claim 25 wherein the hydrocarbylaluminumoxane is an alkylaluminumoxane.
27. A method as in Claim 26 wherein the alkylaluminumoxane is methylaluminumoxane.
28. An ionic aluminoxanate produced by a method of any of Claims 9-27.
29. A composition which comprises an ionic aluminoxanate as in any of Claims 1-3 or 28 supported on an organic or inorganic catalyst support or carrier.
30. A composition as in Claim 29 wherein said catalyst support or carrier is a chemically treated catalyst support or carrier to at least remove hydroxyl groups from the support or carrier.
31. A composition as in Claim 29 wherein said support or carrier is a porous inorganic catalyst support or carrier.
32. A composition as in Claim 31 wherein said inorganic catalyst support or carrier is comprised of a zeolite, magnesium chloride, or at least one inorganic oxide.
33. A composition as in Claim 31 wherein said inorganic catalyst support or carrier is silica, alumina, or silica-alumina.
34. A composition as in Claim 31 wherein said inorganic support or carrier is silica.
35. A composition as in Claim 29 wherein said support or carrier is an organic resinous catalyst support.
36. A method of producing a supported ionic aluminoxanate composition, which method comprises
  - A) thoroughly washing a liquid clathrate formed from (i) an aluminumoxane, (ii) an organic, inorganic, or organometallic compound, and (iii) an aromatic solvent, to form a washed liquid clathrate;

B) forming and mixing a slurry of (a) said washed liquid clathrate, (b) a particulate catalyst support or carrier material, and (c) an inert liquid polar halogenated hydrocarbon solvent, or a liquid aromatic hydrocarbon solvent, capable of dissolving the ionic aluminoxanate composition so that (a) is dissolved or solvated form and (b) come into intimate contact with each other and form a supported ionic aluminoxanate.

37. A method as in Claim 36 wherein (c) is a liquid aromatic hydrocarbon solvent.

38. A method as in Claims 36 or 37 wherein the amount of washing in A) thereof is sufficient such that if and when solids are precipitated from a sample of the washed clathrate from A) by addition of cyclohexane to the sample, the resultant precipitated ionic aluminoxanate solids have an electrical conductivity at 25°C when dissolved to a concentration of 1.67 weight percent in 99.9% A.C.S. HPLC grade, or better, methylene chloride, that is higher than the electrical conductivity, under the same conditions, of the aluminoxane of A) (i) from which the ionic aluminoxanate is derived.

39. A method as in any of Claims 36-38 wherein the amount of washing in A) thereof is sufficient such that if and when solids are precipitated from a sample of the washed clathrate from A) by addition of cyclohexane to the sample, if any aluminum trialkyl is present in the sample, the amount of aluminum as aluminum trialkyl relative to the total aluminum in said sample, is less than 5 mole % as determined by proton NMR.

40. A catalyst composition which comprises a composition formed from interaction between components comprising (i) an aluminoxanate as in any of Claims 1-3 or 28, and (ii) at least one catalyst compound or complex of a transition metal including the lanthanide series and the actinide series.

41. A catalyst composition as in Claim 40 wherein component (ii) is a compound or complex of a late transition metal.

42. A catalyst composition as in Claim 40 wherein component (ii) is a metallocene.

43. A catalyst composition as in Claim 42 wherein the metallocene is a metallocene of a Group 4-6 metal.

44. A catalyst composition as in Claim 42 wherein the metallocene is a metallocene of a Group 4 metal.

45. A catalyst composition as in Claim 42 wherein the metallocene is a metallocene having constrained geometry.

46. A catalyst composition as in Claim 45 wherein the metallocene is a metallocene of titanium.

47. A catalyst composition as in Claim 40 wherein component (ii) is a Ziegler-Natta catalyst compound.

48. A process of producing an olefin polymer, which process comprises polymerizing at least one polymerizable olefinic monomer in the presence of a catalyst composition as in any of Claims 40-47.

49. A process as in Claim 48 wherein ethylene or propylene is subjected to homopolymerization or wherein at least ethylene and at least one alpha-olefin having in the range of 3 to about 8 carbon atoms are subjected to copolymerization.

50. An ionic aluminoxanate composed of (i) a stabilized dialkylaluminum cation of the formula  $[L_nR_2Al]^{\oplus}$ , where L is a stabilizing ligand, each R is, independently, an alkyl group having up to about 20 carbon atoms and n is 1 when L is a bidentate ligand and 2 when L is a monodentate ligand; and (ii) an aluminoxanate anion of the formula  $[(RAO)X]^{\ominus}$ , where RAO is an alkylaluminoxane in which the alkyl group has up to about 20 carbon atoms and is the same or different from the alkyl group of said cation, and wherein X is an alkyl group which is the same or different from the alkyl group of the cation.

51. An ionic aluminoxanate of Claim 50 wherein the alkyl groups of said cation and of said anion are, independently, either a methyl group or an ethyl group.

52. An ionic aluminoxanate of Claim 50 wherein all of the alkyl groups of said cation and of said anion are methyl groups.

53. An ionic aluminoxanate as in any of Claims 50-52 wherein L is a ligand which is a (i) monosiloxane, (ii) polysiloxane, (iii) monoether, (iv) polyether, (v) monothioether, (vi) a polythioether, or (vii) a crown ether having oxygen, nitrogen, phosphorus, or sulfur coordinating atoms therein or a combination of two or more of such coordinating atoms.

54. An ionic aluminoxanate as in any of Claims 50-53 wherein the ligand is a monosiloxane or a polysiloxane and wherein said composition is characterized by a downfield shift of the ligand peak in  $^{29}Si$  NMR of at least 5 ppm and at least 0.2 ppm downfield shift in  $^1H$  NMR.

55. An ionic aluminoxanate as in any of Claims 50-54 wherein said composition is further characterized by (i) a  $^{27}Al$  NMR with at least one large and broad peak shifted upfield from the parent aluminoxane peak, and (ii) at least one smaller peak shifted downfield from the parent aluminoxane peak.

56. An ionic aluminoxanate as in any of Claims 50-55 wherein said composition is further characterized by at least a ten micro-mhos increase in conductivity compared to the parent aluminoxane.

57. A catalyst composition as in any of Claims 40-47 wherein said catalyst is supported on an organic or inorganic catalyst support or carrier.

58. A self-supported catalyst formed by a process which comprises:  
I) mixing together components comprised of (A) at least one catalyst compound or complex of a transition metal including the lanthanide series and the actinide series,

and (B) a viscous liquid composed of ionic aluminoxanate and included aromatic solvent; and

II) recovering a self-supported catalyst from the mixture formed in I);

wherein said viscous liquid of (B) is formed by a process which comprises thoroughly washing one or more times with an aromatic solvent, a liquid clathrate formed from (i) an aluminoxane, (ii) an effective amount of an organic, inorganic, or organometallic compound, and (iii) an aromatic organic solvent, each washing forming a two-phase system composed of a lower layer of a viscous liquid composed of ionic aluminoxanate and included aromatic solvent, and an upper layer of a less dense liquid, and each time removing and discarding the layer of less dense liquid such that a viscous liquid remains.

59. A self-supported catalyst as in Claim 58 wherein the self-supported catalyst is recovered from said mixture formed in I) by a procedure comprising (a) adding to or mixing with the mixture formed in I) a non-solvent to precipitate self-supported catalyst as solids, and recovering said solids by use of a physical solids/liquid separation procedure, or (b) subjecting the mixture formed in I) to vacuum distillation to remove the included aromatic solvent from said mixture, or (c) by spray drying said solids or said mixture formed in I).

60. A self-supported catalyst formed by a process which comprises interacting components comprised of (A) at least one catalyst compound or complex of a transition metal including the lanthanide series and the actinide series, and (B) an ionic aluminoxanate as in any of Claims 1, 2, 3, 28, 50, 51, 52, 53, 54, 55, or 56, said interacting being conducted in an inert solvent or diluent when (A) and (B) are solids.

61. A self-supported catalyst as in any of Claims 58-60 wherein said aluminoxanate is derived from a C<sub>1-6</sub> alkylaluminoxane.

62. A self-supported catalyst as in Claim 61 wherein said C<sub>1-6</sub> alkylaluminoxane is methylaluminoxane.

63. A method of producing a self-supported catalyst, which method comprises:

I) mixing together components comprised of (A) at least one catalyst compound or complex of a transition metal including the lanthanide series and the actinide series, and (B) a viscous liquid composed of ionic aluminoxanate and included aromatic solvent; and

II) recovering a self-supported catalyst from the mixture formed in I);

wherein said viscous liquid of (B) is formed by a process which comprises thoroughly washing one or more times with an aromatic solvent, a liquid clathrate formed from (i) an aluminoxane, (ii) an effective amount of an organic, inorganic, or organometallic compound, and (iii) an aromatic organic solvent, each washing forming a two-phase system composed of a lower layer of a viscous liquid composed of ionic aluminoxanate and included aromatic solvent, and an upper layer of a less dense liquid, and each time removing and discarding the

layer of less dense liquid such that a viscous liquid remains.

62. A method as in Claim 61 wherein the self-supported catalyst is recovered from said mixture formed in I) by a procedure comprising (a) adding to or mixing with the mixture formed in I) a non-solvent to precipitate self-supported catalyst as solids, and recovering said solids by use of a physical solids/liquid separation procedure, or (b) subjecting the mixture formed in I) to vacuum distillation to remove the included aromatic solvent from said mixture, or (c) by spray drying said solids or said mixture formed in I).

63. A method of producing a self-supported catalyst, which method comprises interacting components comprised of (A) at least one catalyst compound or complex of a transition metal including the lanthanide series and the actinide series, and (B) an ionic aluminoxanate as in any of Claims 1, 2, 3, 28, 50, 51, 52, 53, 54, 55, or 56, said interacting being conducted in an inert solvent or diluent when (A) and (B) are solids.

# DiMethylAluminum Methaluminoxanate

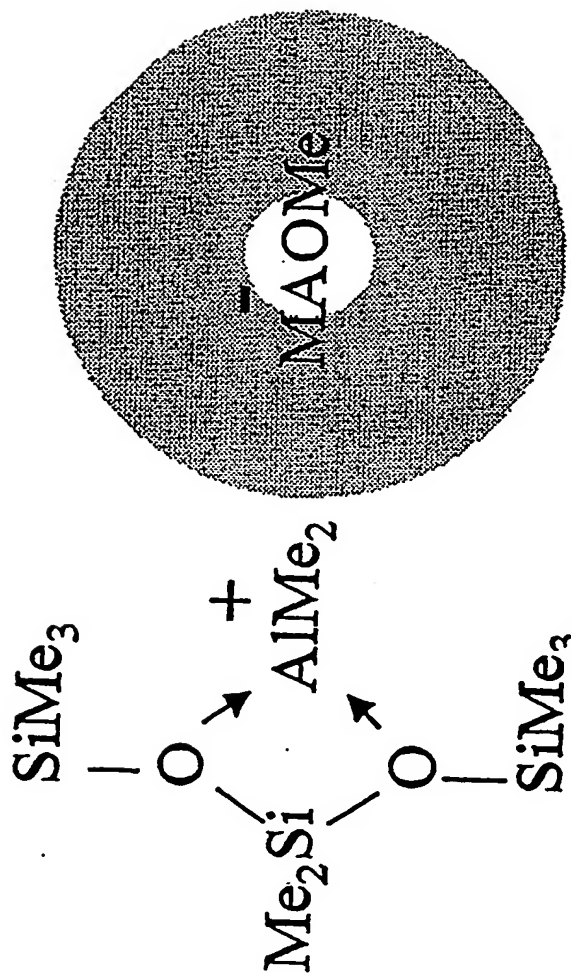
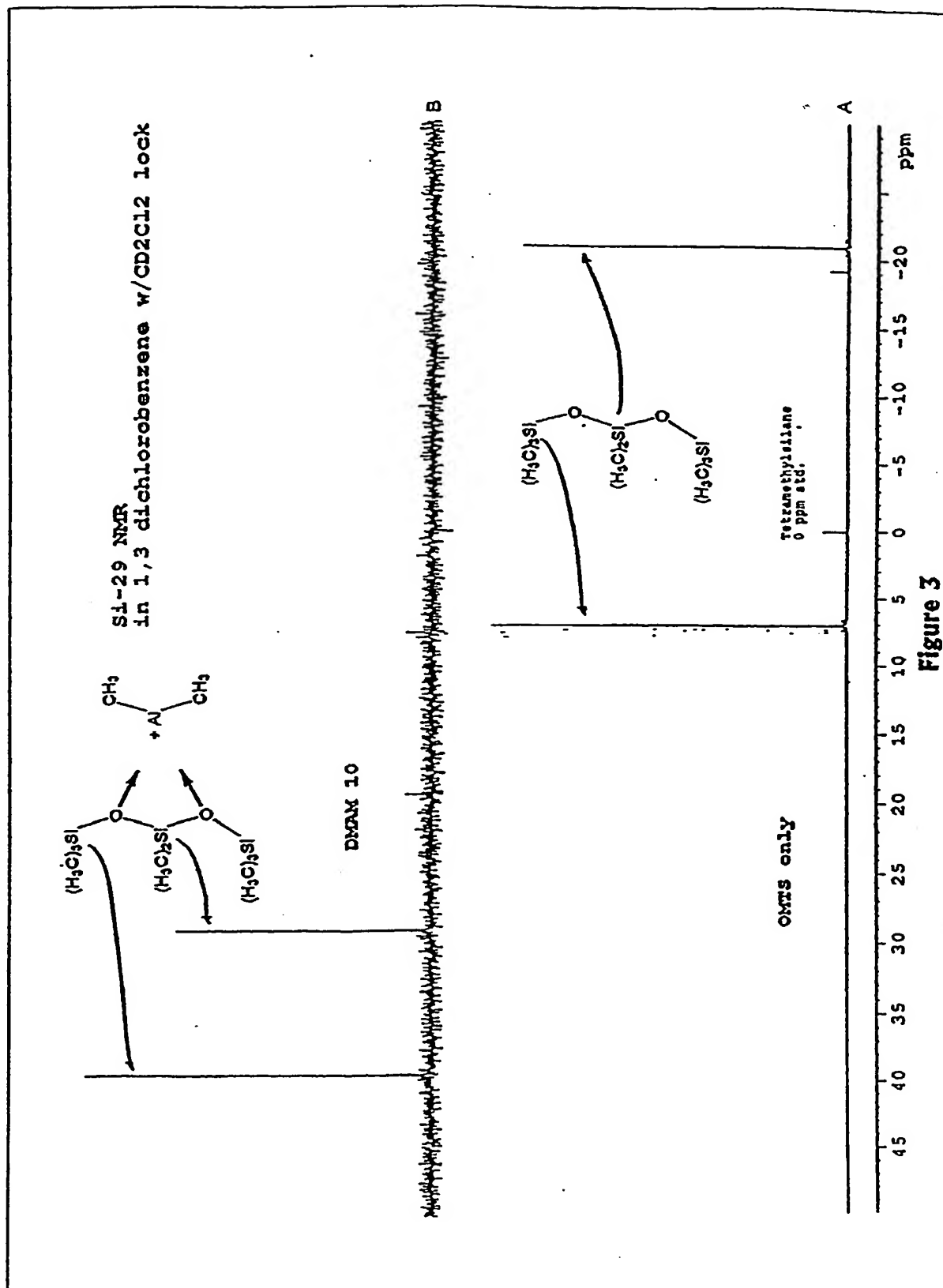
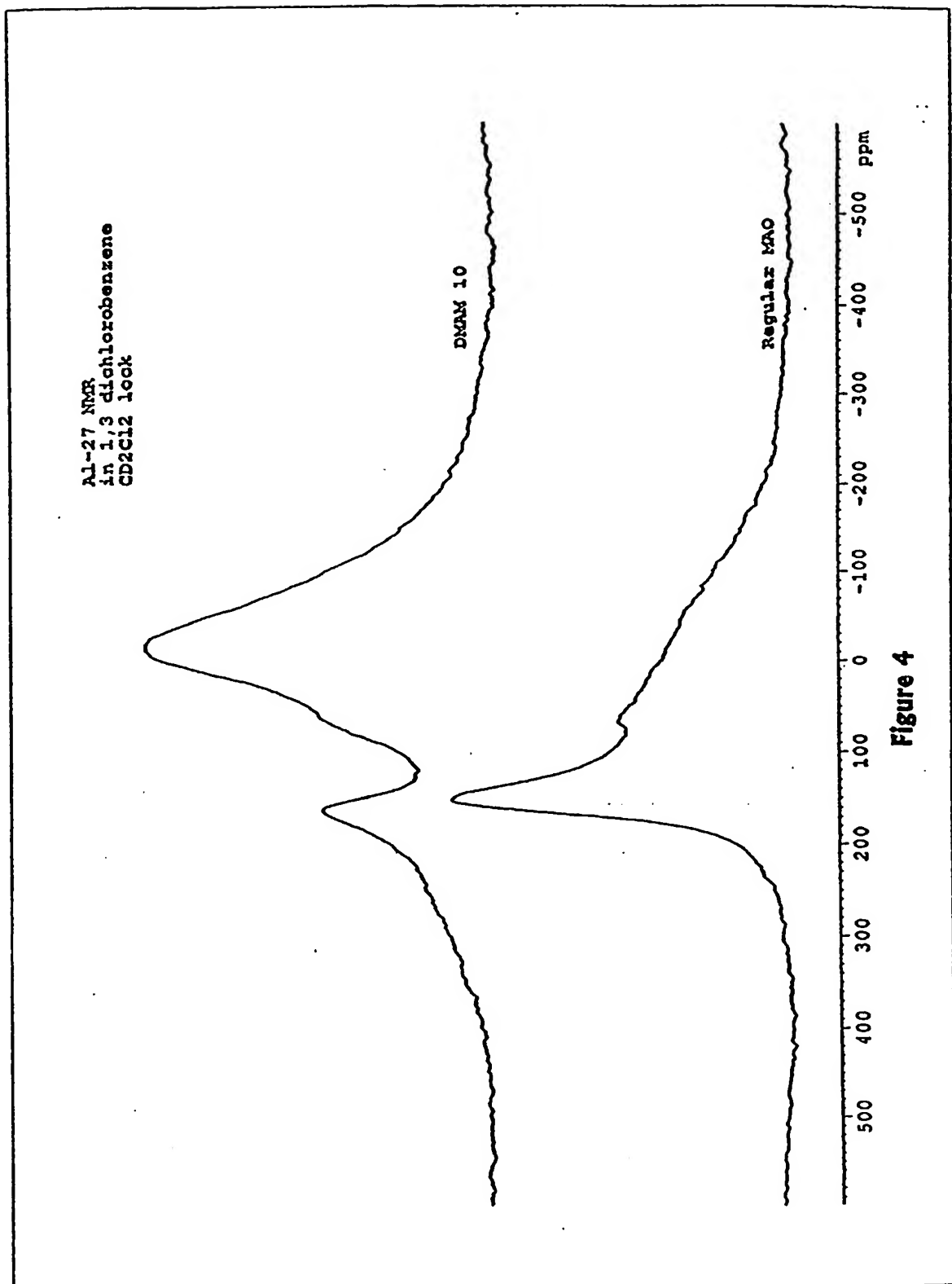


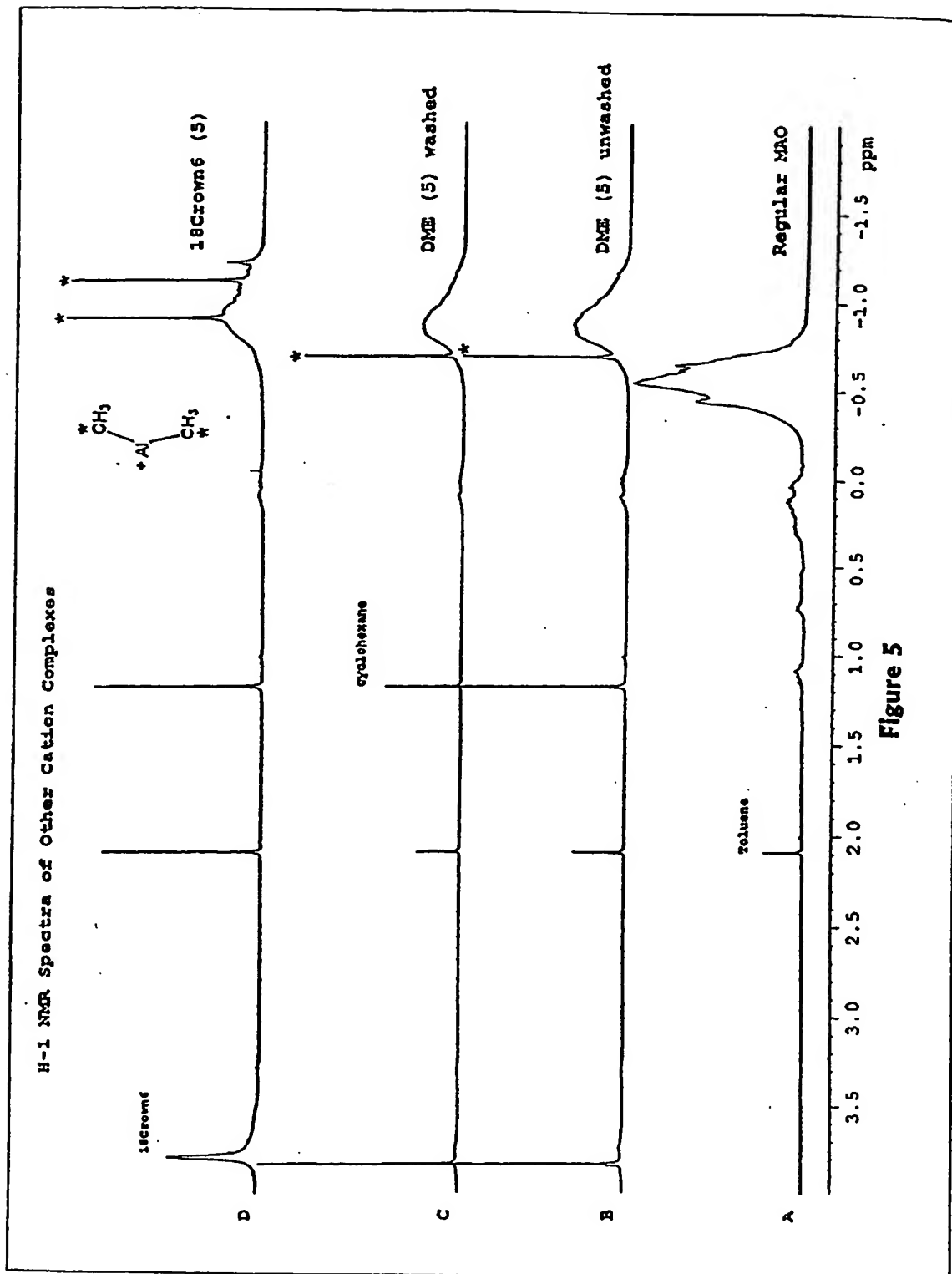
Figure 1











Ethylene Polymerization Runs with Silica-supported Iron Catalyst:  
DMAM versus MAO as Activator. (60 & 80°C)

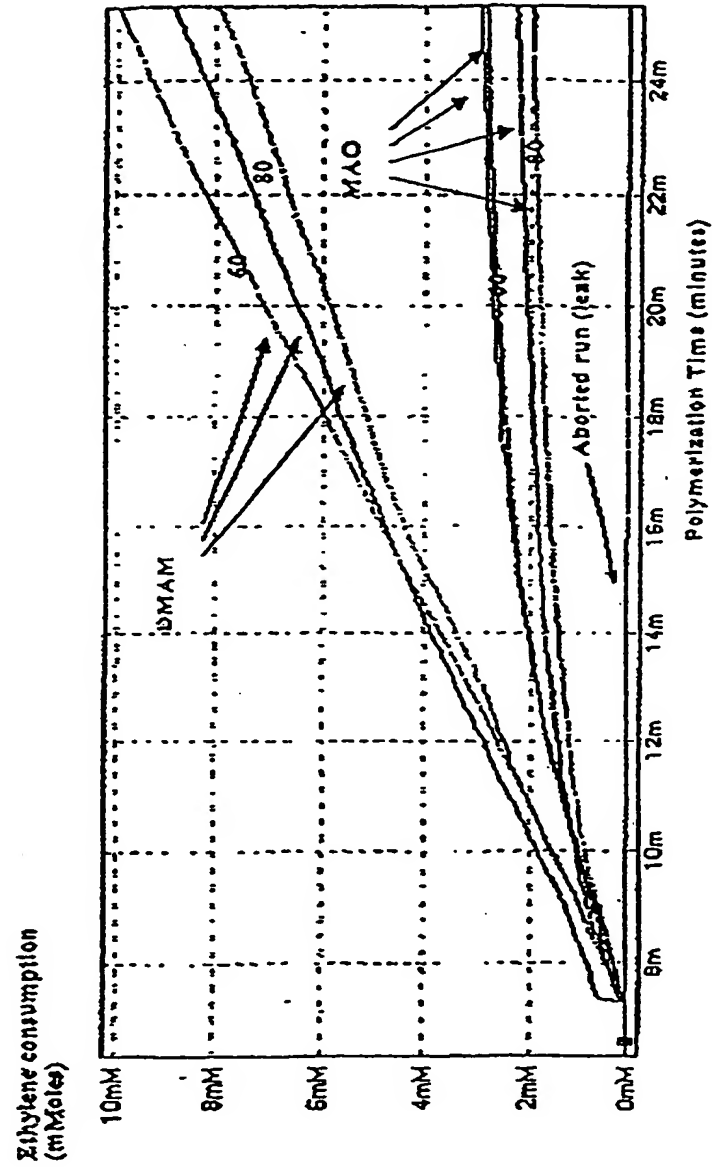


Figure 6

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 03/09567

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F5/06 C07F7/08 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 755 936 A (ALBEMARLE CORPORATION) 25 July 1995 (1995-07-25) the whole document -----	1-65



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

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\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

23 June 2003

Date of mailing of the international search report

04/07/2003

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